Dauben.[7] The lattice parameters of Tm_2Se_3 and Lu_2Se_3 are somewhat larger than would be predicted from a straight-line extrapolation of the lighter rare earths, and this same effect has been previously observed for the sesquisulfides. The lattice parameter of Yb_2Se_3 is somewhat greater than its neighbors which indicates some Yb^{2+} character in Yb_2Se_3. This same effect was also observed in Yb_2S_3.[2] A graph of the minumum pressure for synthesis of the cubic polymorphs as a function of ionic radius of the rare earth is shown in Figure 2. Values for Ho_2Se_3 and Er_2Se_3 were taken from Eatough, Webb, and Hall.[2] The synthesis of Ho_2Se_3, Er_2Se_3, and Tm_2Se_3 takes place at about the same pressure. According to Gschneidner and Valletta[8] if the pressure required for synthesis increases with atomic number of the rare earth, there is 4f-electron participation in the chemical bonding. If the pressure required decreases with increasing atomic number, the crystal structure of the compound is determined by size effects only. In the sesquiselenide series there seems to be a combination of size effect and 4f-electron bonding determining the structure for the cubic polymorphs of Ho, Er, and Tm. For Yb and Lu the 4f bonding becomes increasingly important.

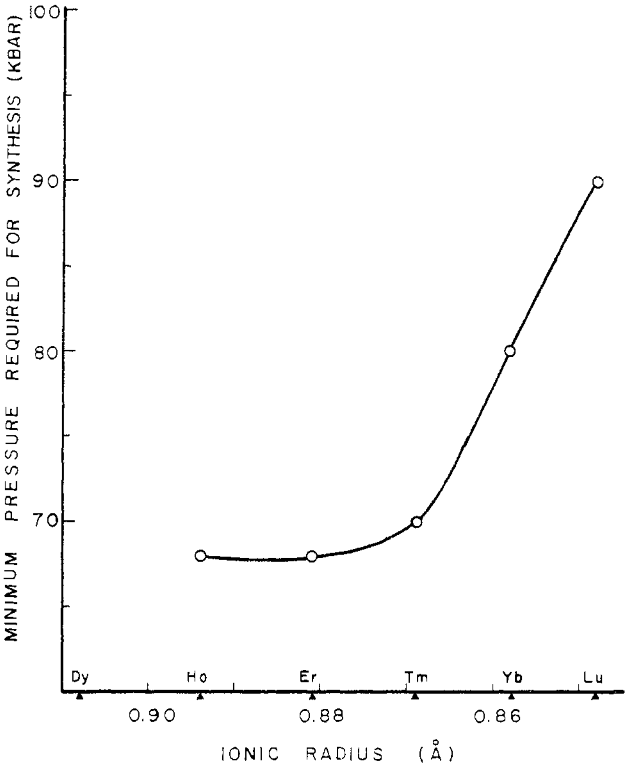

Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

Acknowledgments.—Thanks are extended to the Army Research Office (Durham) for financial support during this research.

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[8] K. A. Gschneidner, Jr., and R. M. Valletta, *Acta Met.*, **16**, 477 (1968).

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Stereochemistry of β-Diketone Complexes of Cobalt(III). III. *cis* and *trans* Isomers of Nitroaminebis(acetylacetonato)cobalt(III)[1]

By L. J. Boucher and Nyole G. Paez

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The reaction of the anion[2] *trans*-$Co(acac)_2(NO_2)_2^-$ with a variety of amines leads rapidly to the exclusive formation of a *trans* product *via* the scheme[3-5]

$$\textit{trans}\text{-Co(acac)}_2(\text{NO}_2)_2^- + \text{H}_2\text{O} \rightleftarrows \textit{trans}\text{-Co(acac)}_2\text{NO}_2\text{H}_2\text{O} + \text{NO}_2^-$$

$$\textit{trans}\text{-Co(acac)}_2\text{NO}_2\text{H}_2\text{O} + \text{amine} \longrightarrow \textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}) + \text{H}_2\text{O}$$

The above reactions appear to be an example of the octahedral *trans* effect of the nitro ligand. Although a previous study[3] did not report an amine-exchange reaction, more careful work reveals that this reaction does occur rapidly at elevated temperatures as[6]

$$\textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}) + \text{amine}' \rightleftarrows \textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}') + \text{amine}$$

Thus the nitro ligand exerts a general rather than a specific *trans* effect in these complexes. In the course of studying the kinetics of amine-exchange reactions, we have observed the formation of several new complexes. We wish to report here the preparation and characterization of the previously unknown *cis* isomers of the amine complexes with the two representative amines pyridine and 4-*t*-butylpyridine.

Experimental Section

Synthesis of Complexes.—Na[*trans*-$Co(acac)_2(NO_2)_2$] was prepared as previously described.[1] Reagent grade pyridine and 4-*t*-butylpyridine (Reilly Tar and Chemical Co.) were used without further purification.

trans-**$Co(acac)_2NO_2$(amine).**—Five grams of Na[*trans*-$Co(acac)_2(NO_2)_2$] (0.013 mol) was dissolved in 100 ml of distilled water, and 3.2 g of pyridine (0.040 mol) or 5.4 g of 4-*t*-butylpyridine (0.040 mol) was added to the solution. In order to prevent formation of an oily product, 25 ml of methanol was added to the latter solution. The resulting mixture was stirred at 25° for 1 hr and then filtered. The red-brown solid was washed with two 50-ml portions of distilled water, a little acetone, and then ether and air dried. The yield was 4.3 and 4.9 g, respectively, 85% based on the original cobalt complex.

Anal.[7] Calcd foi $C_{15}H_{19}O_6N_2Co$ [$Co(acac)_2NO_2py$]: C, 47.13; H, 5.01; N, 7.33. Found: C, 46.89; H, 4.97; N, 7.33 (mp 169°). Calcd for $C_{19}H_{26}O_6N_2Co$ [$Co(acac)_2NO_2bpy$]: C, 52.18;

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] Abbreviations used in this paper include: acac, 2,4-pentanedionato (acetylacetonato); py, pyridine; bpy, 4-*t*-butylpyridine.

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[5] R. D. Archer and B. P. Cotsoradis, *ibid.*, **4**, 1584 (1965).

[6] L. J. Boucher and E. P. McGovern, unpublished results.

[7] Elemental Analyses by Galbraith Laboratories, Inc., Knoxville Tenn.

H, 5.79; N, 6.40. Found: C, 52.35; H, 6.00; N, 6.31 (mp 172°).

***cis*-Co(acac)$_2$NO$_2$(amine).**—Two grams of *trans*-Co(acac)$_2$NO$_2$(amine) was dissolved in 100 ml of chloroform and the resulting solution was refluxed for 3 hr. The reaction mixture was filtered (little or no residue) and the filtrate was reduced to dryness in an air stream. A portion of the red solid, which contains a mixture of the *cis* and *trans* isomers with a trace of fast-moving and unknown yellow and green materials, was separated by thin layer chromatography. However, no side products are noted when the solutions are heated in the absence of air. A solution of the solid, 0.2 g in 8 ml of chloroform, was placed on 20 cm × 20 cm plates coated to a 0.25-mm thickness with silica gel F-254 (Brinkmann Instruments). The plates were developed with 25% methanol–benzene for 1 hr. The R_f values based on one development of approximately 15 cm are: *cis*-py, 0.73; *trans*-py, 0.60; *cis*-bpy, 0.81; *trans*-bpy, 0.69. The *cis* isomer was removed from the plate by scraping off the spot and then extracting the complex from the silica gel with methanol. After the methanol was stripped off *in vacuo* at room temperature, the residue was recrystallized from chloroform–petroleum ether (bp 30–60°) and air dried. A typical yield of the *cis* isomer is ~0.06 g, 30% recovery.

Anal. Calcd for $C_{15}H_{19}O_6N_2Co$ [Co(acac)$_2$NO$_2$py]: C, 47.13; H, 5.01; N, 7.33. Found: C, 47.27; H, 5.01; N, 7.26 (mp 172°). Calcd for $C_{19}H_{26}O_6N_2Co$ [Co(acac)$_2$NO$_2$bpy]: C, 52.18; H, 5.99; N, 6.40. Found: C, 52.15; H, 6.15; N, 6.31 (mp 175°).

Spectral Measurements—Ultraviolet and visible spectra were obtained with a Cary 14 recording spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 237 spectrophotometer in the 4000–260-cm^{-1} range, with the materials in potassium bromide pellets. Nuclear magnetic resonance spectra were obtained at 34° with a Hitachi Perkin-Elmer Model R-20 60-MHz spectrometer.

Results and Discussion

Although the isomerization of the *trans* complex is slow at room temperature, at slightly elevated temperatures (~60°) the equilibrium

$$trans\text{-Co(acac)}_2\text{NO}_2\text{(amine)} \rightleftharpoons cis\text{-Co(acac)}_2\text{NO}_2\text{(amine)}$$

is established in a few hours. Furthermore the same mixture is formed from the *cis* complex as from the *trans* complex. The formation of the *cis* isomer appears to be slightly favored. Isomerization is more rapid at higher temperatures, *i.e.*, in refluxing benzene, toluene, etc. Under these conditions, however, undesirable decomposition products build up.

The mixture of the *cis* and *trans* isomers can be fractionated in a number of ways. For example, fractional crystallization of the pyridine complex enriches the mother liquor in the more soluble *cis* isomer. Fortunately, the crystal habits of these isomers are different. The dark brown cubic crystals of the *trans* complex can be manually separated from the feathery needlelike red crystals of the *cis* isomer. Of all the methods tried, thin layer chromatography on silica gel offers the most rapid and satisfactory way of isolating the pure *cis* isomer. Wet or dry column chromatography on alumina, Florisil, or silica gel does not result in a clean isomer separation. Interestingly enough, if the *cis* complex is left on the tlc plate overnight, it partially reisomerizes. Once isolated, the isomer pairs appear to be stable toward isomerization at room temperature in solution for many hours.

Nuclear magnetic resonance spectroscopy provides the best method of establishing the identity of the isomer pairs.[8] A typical nmr spectrum of the *cis* and *trans* isomers is shown in Figure 1 and the proton chemical shifts for all the complexes are given in Table I. The assignments are based on those given for many other acetylacetone–cobalt complexes.[3–5, 9] It is readily seen that the spectra are distinguishable for the pyridine complex; *e.g.*, the *trans* isomer shows only one γ-C–H (relative intensity 1) resonance and one CH$_3$ (intensity 6) resonance while the *cis* isomer shows two γ-C–H lines (1:1) and four CH$_3$ lines (3:3:3:3). The *trans* spectrum is consistent with the fact that all the methyl groups in the complex are equivalent (related by a symmetry element). On the other hand, all the methyl groups are in nonequivalent sites in the *cis* isomer and the *cis* spectrum shows four different chemical shifts. A similar argument is made for the γ-C–H proton. Observation of different chemical shifts rests upon either differing intermolecular or intramolecular interactions (solvation) for the various protons in the complex.[10] The former can involve ring anisotropy effects due to the ring current of the coordinated pyridine and of the acetylacetone chelate ring. Since the chelate ring current is very small,[11] only the pyridine need be considered. One set of methyl groups could lie in the plane of the pyridine ligand and would be deshielded. A second set of methyl groups could lie perpendicular to the π cloud of the pyridine and would be shielded. Since the pyridine ligand should freely rotate about the cobalt–nitrogen bond, it is difficult to assign the proton resonance specifically since all the methyl groups could be alternately shielded or deshielded. The difference in chemical shifts of the γ-C–H protons can be ascribed to differing interactions of the planar nitro and pyridine ligands with the two chelate rings. The monodentate ligands must be in the plane of one chelate ring and

TABLE I

PROTON CHEMICAL SHIFTS FOR COMPLEXES[a]

Co(acac)$_2$NO$_2$py		Co(acac)$_2$NO$_2$bpy		
cis	*trans*	*cis*	*trans*	Assignment
		−1.32	−1.27	*t*-Butyl
−2.02		−2.01		–CH$_3$
−2.15	−2.13	−2.14	−2.03	
−2.19		−2.21		
−2.21				
−5.35	−5.32	−5.40	−5.23	C–H
−5.57		−5.56		
−7.22	−7.40	−7.24	−7.20	Pyridine
−7.42	−7.51	−7.36	−7.26	
−7.64	−7.71	−8.32	−8.24	
−7.77	−7.87	−8.43	−8.37	
−8.48	−8.46			
−8.57	−8.55			

[a] Chemical shifts, ppm, relative to tetramethylsilane; ~5% (w/v) solutions in CDCl$_3$.

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(8) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(9) B. P. Cotsoradis and R. D. Archer, *ibid.*, **6**, 800 (1967).

(10) R. J. York, W. D. Bonds, B. P. Cotsoradis, and R. D. Archer *ibid.*, **8**, 789 (1969).

(11) N. Serpone and R. C. Fay, *J. Am. Chem. Soc.*, **90**, 5701 (1968).

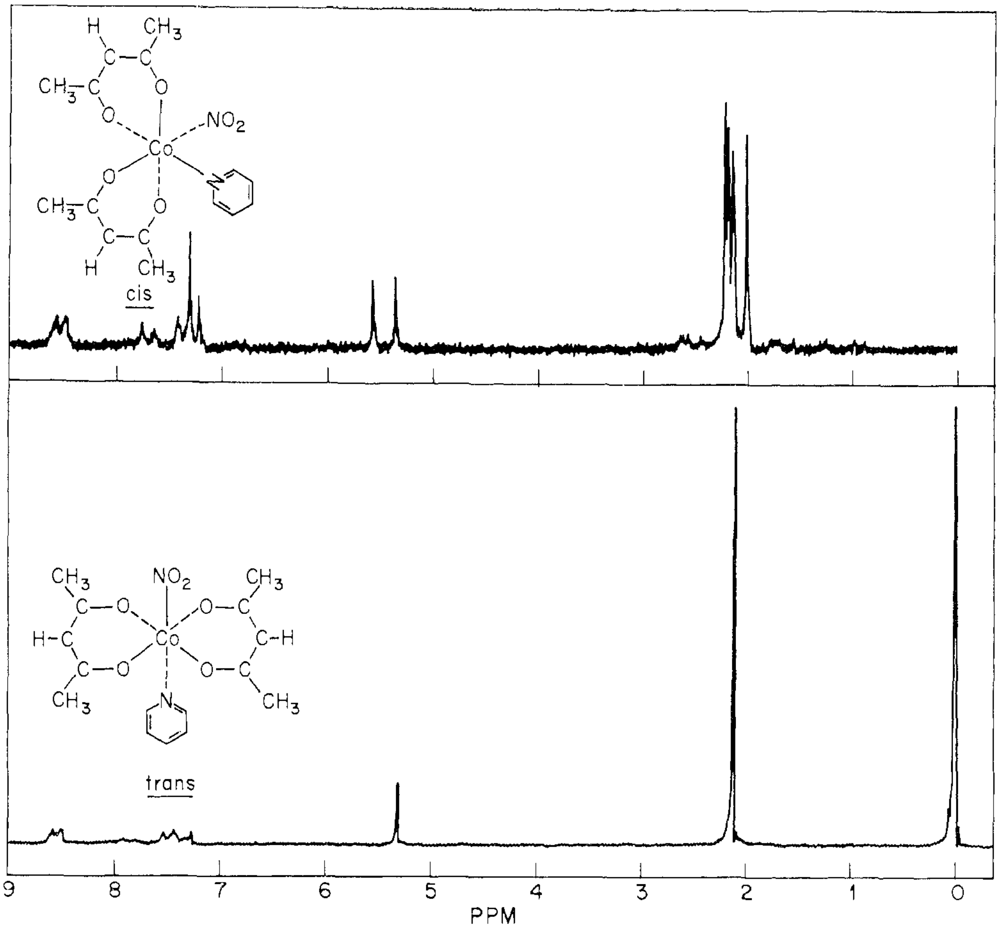

Figure 1.—Proton magnetic resonance spectrum for *cis*- and *trans*-nitropyridinebis(acetylacetonato)cobalt(III) in deuteriochloroform.

perpendicular to the other ring. Solvation effects undoubtedly also could lead to similar splittings. The total spread in CH_3 resonance is moderate and is greater than for the dinitro case[9] and much less than for the bipyridine case.[5] Observations similar to those for the pyridine complex are made for the butylpyridine complex. The *trans* isomer shows only one methyl (intensity 6) and one γ-C–H resonance (intensity 1) while the *cis* isomer shows three methyl resonances (6:3:3) and two γ-C–H resonances (1:1). The small splitting of two of the methyl group resonances does not appear to be resolved in the *cis* isomer of the butylpyridine case. Solvation effects related to the bulky *t*-butyl group may account for this. In addition to the acetylacetone proton resonances, the spectra show those arising from the pyridine protons. The ring protons give a number of lines in the −7.20 to −8.60 ppm region and the *t*-butyl protons give a single line in the −1.32 to −1.27 ppm region. In general the pyridine resonances of the *cis* isomer lines are shifted upfield from those of the *trans* isomer.

In addition to nmr spectra, the infrared and uv–visible spectra of the complexes were studied. The infrared spectra of the pairs of isomers are similar and resemble the spectra of those previously reported[3,4] for the *trans* complexes. The only obvious differences occur in the low-frequency region, 850–250 cm^{-1}, and here there are only slight frequency shifts and some moderate relative intensity differences for the isomer pairs. The electronic spectra of the complexes are summarized in Table II. The assignment follows from those made previously for similar complexes.[10] A shoulder is also seen at ~26 kK which can be assigned to the $^1A_{1g} \rightarrow {}^1T_{2g}$ cobalt transition. The high-energy $\pi \rightarrow \pi^*$ transition is obscured by solvent absorption. For the *cis* isomers the d → d bands are at lower energy than for the *trans* isomer. Conversely, the charge-transfer band and the ligand band are at higher energy for the *cis* than for the *trans* isomer. Although the opposite energy order is observed[5] for the *cis*- and *trans*-$Co(acac)_2(NH_3)_2^+$, the same order is observed[9] for *cis*- and *trans*-$Co(acac)_2(NO_2)_2^-$. It is interesting to note that the intensity of the ligand field band is slightly higher for the *cis* isomers in agreement with the notion that the lower symmetry isomer is expected to have the

Table II

Visible and Ultraviolet Spectra[a] of $Co(acac)_2NO_2(amine)$ Isomers

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$	$t_{2g} \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
cis-py	18.6 (2.25)	30.9 sh	38.3 (4.45)
trans-py	18.7 (2.22)	30.3 sh	37.7 (4.45)
cis-bpy	18.5 (2.25)	30.8 sh	38.5 (4.44)
trans-bpy	18.8 (2.21)	29.9 sh	37.8 (4.45)

[a] All peak positions are given in kilokaisers; log ε values are in parentheses; chloroform solutions.

higher intensity bands. Finally, there is no observable splitting of the d → d band for either isomer.

The mechanism of the *cis* → *trans* isomerization is not known. In order to learn something more about this interesting reaction, we are currently studying the thermodynamics and kinetics of the isomerization.

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Preparation of Stannic Chloride Sulfide

BY CHRISTIAN H. STAPFER

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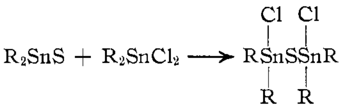
The reaction of dialkyltin sulfides with corresponding dialkyltin dichlorides is known to involve halogen transfer yielding 1,1,3,3-tetraalkyl-1,3-dichlorodistanthianes[1,2]



$$R_2SnS + R_2SnCl_2 \longrightarrow R\overset{Cl}{\underset{R}{Sn}}S\overset{Cl}{\underset{R}{Sn}}R$$

When $SnCl_4$ is used in place of R_2SnCl_2, a more complex reaction is observed,[3] *i.e.*

$$3(C_4H_9)_2SnS + 2SnCl_4 \longrightarrow 3(C_4H_9)_2SnCl_2 + Sn_2Cl_2S_3$$

The resulting $Sn_2Cl_2S_3$ is a white, reactive solid which is amorphous to X-rays. It reacts with water forming H_2S and uncharacterized oxides and oxychlorides. It is unstable in air or in inert atmosphere and decomposes rapidly into stannic sulfide and $SnCl_4$

$$2SnCl_2S_3 \xrightarrow{\Delta} 3SnS_2 + SnCl_4$$

The character of the new compound was not affected by varying the ratio of dibutyltin sulfide and $SnCl_4$. An excess of $(C_4H_9)_2SnS$ leads to the formation of 1,1,3,3-tetrabutyl-1,3-dichlorodistanthiane along with dibutyltin dichloride and $Sn_2Cl_2S_3$.

Experimental Section

In a modular drybox containing a nitrogen atmosphere, 7.95 g of pure di-*n*-butyltin sulfide, prepared from recrystallized di-*n*-butyltin dichloride and sodium sulfide following the reported procedure,[4] was dissolved into 50 ml of anhydrous *n*-hexane. Slowly and under magnetic agitation, 5.21 g of reagent grade stannic chloride was added to this solution. After 15 minutes of vigorous agitation at room temperature, the white precipitate was filtered, washed several times with hexane, and vacuum dried; yield, 3.92 g. *Anal.* Calcd for $Sn_2Cl_2S_3$: Sn, 58.6; Cl, 17.5; S, 23.7. Found: Sn, 56.9; Cl, 17.0; S, 24.0. A 2.8-g amount of di-*n*-butyltin dichloride was recovered by evaporation of the filtrate. When $Sn_2Cl_2S_3$ was heated in a crucible at 120° until the evolution had subsided, a quantitative amount of SnS_2 was recovered.

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Organotin Sulfates from the Oxidation of Organotin Sulfides with Hydrogen Peroxide

BY CHRISTIAN H. STAPFER AND ROBERT D. DWORKIN

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The subject of this paper is the investigation of the reaction of aqueous hydrogen peroxide with *n*-butyl-substituted stannyl sulfides which led to the preparation of several organotin sulfate derivatives. The preparation of bis(trialkyltin) sulfates either by ester-exchange reactions of trialkyltin mercaptides[1] or by reaction of sodium hydrosulfate with bis(trialkyltin) oxides or hydroxides[2] has been previously described. It is also known that acyl peroxides and esters of some peracids react with various organometallic compounds, in particular triethyltin halides[3,4] and bis(triethyltin) sulfide.[5] In the latter case, benzoyl peroxide was shown to cleave both tin–sulfur bonds of the organotin sulfide to form triethyltin benzoate and elemental sulfur. No other work has been reported on the oxidation of the tin–sulfur bonds of organotin sulfides.

Experimental Section

Bis(tri-*n*-butyltin) Sulfate.—To a solution of 30.6 g (0.05 mol) of pure bis(tri-*n*-butyltin) sulfide in 50 ml of *n*-hexane was added dropwise under vigorous agitation 9.7 g (0.1 mol) of a 35% aqueous solution of hydrogen peroxide. After maintaining the agitation at room temperature until all peroxide had been consumed (potassium iodide test), the water was eliminated by azeotropic distillation. The remaining white precipitate was filtered, washed with hexane, and dried under vacuum over calcium chloride. Twenty-seven grams of pure bis(tri-*n*-butyltin) sulfate melting at 140–144° was obtained in 80% yield. *Anal.* Calcd for $C_{24}H_{54}O_4SSn_2$: C, 42.63; H, 8.05; O, 9.47; S, 4.74; Sn, 35.11. Found: C, 41.72; H, 8.13; O, 10.00; S, 4.69; Sn, 35.39. Infrared spectrum [potassium bromide wafer on Perkin-Elmer Infracord 337 grating spectrometer (in cm^{-1})]: 2900 (vs), 1450 (s), 1270 (s), 1100 (vs), 870 (w), 665 (v), 620 (s), 520 (vw), 470 (vw).

Di-*n*-butyltin Sulfate.—Fifty-seven grams (0.1 mol) of pure, recrystallized bis(chlorodi-*n*-butyltin) sulfide, prepared by heating at 100° for 1 hr equimolar amounts of di-*n*-butyltin sulfide and di-*n*-butyltin dichloride and recrystallized from *n*-hexane, was dissolved in 100 ml of *n*-hexane. To this solution, 19.5 g (0.2 mol) of 35% aqueous hydrogen peroxide was added dropwise under agitation. The agitation was maintained until completion of the reaction and the water was eliminated by azeotropic distil-

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