Synthesis of Dihalogenobis(2-pyridinethiolato)tin(IV) by the Oxidative Addition of Disulfide to Tin(II) Halides—Consideration on the Coordination Structure[1]

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The reaction of di-2-pyridyl disulfide with tin(II) halides was found to give dihalogenobis(2-pyridinethiolato)-tin(IV). The oxidative addition reaction was successfully extended to the preparation of other dihalogenodithiolatotin(IV) complexes. Dichlorobis(2-pyridinethiolato)tin(IV) was also prepared by the reaction of 2(1*H*)-pyridinethione with tin(IV) chloride and proposed to be a monomeric, octahedral complex with a four-membered (Sn, S, C, and N) chelate ring from its molecular weight and IR spectral data. Dichlorobis(2-quinolinethiolato)tin(IV) could be isolated similarly as a stable complex. However, attempts to isolate the dichlorodithiolatotin(IV) in which an intramolecular chelation seems hardly possible were unsuccessful. The great stability of bis(2-pyridinethiolato)- and bis(2-quinolinethiolato)-dihalogenotin(IV) could be ascribed to the intramolecular four-membered chelate ring formation for the six-coordination of tin atom.

In a previous paper, an isolation of a stable complex, dichlorobis(2-pyridinethiolato)tin(IV) (**1**) was reported.[2] Several types of stable dihalogenodithiolatotin(IV) complexes, formed with dithiocarbamato,[3] phosphinodithionito,[4] alkoxycarbonylmethanethiolato,[5] 1,3-diphenyl-3-thioxo-1-propanonato[6] and 2-pyridinethiolato *N*-oxide[7] are known. These ligands act as a bidentate in the complexes and allow the intramolecular chelation for six-coordination of tin atom. Six-membered (Sn, S, 3 C, and O), five-membered (Sn, S, C, C or N, and O) and four-membered (Sn, S, C or P, and S) chelate ring structures have been proposed for the complexes. Six-coordination of the tin atom seems possible for the complex **1** by a coordination of the pyridine nucleus through nitrogen. Such a coordination, however, would lead to the formation of a new type four-membered (Sn, S, C, and N) chelate ring.

This paper deals with the synthesis of dihalogenobis(2-pyridinethiolato)tin(IV) by the oxidative addition reaction of di-2-pyridyl disulfide to tin(II) halides, an extension of the reaction to prepare other dihalogenodithiolatotin(IV) complexes, and an observation on the structure of **1**, as well as a consideration on a relationship between the stability of dihalogenodithiolatotin(IV) complex and its coordination structure.

Results and Discussion

Synthesis. When tin(II) chloride was mixed with an equimolar or excess amount of di-2-pyridyl disulfide in an organic solvent such as 1,2-dichloroethane or benzene at room temperature, an exothermic reaction occurred and dichlorobis(2-pyridinethiolato)-tin(IV) (**1**) was produced in a high yield. The product was identified by IR spectrum with the specimen prepared from the reaction of 2(1*H*)-pyridinethione with tin(IV) compounds. Analogous reactions of the disulfide with tin(II) bromide and tin(II) iodide afforded dibromobis(2-pyridinethiolato)tin(IV) and diiodobis(2-pyridinethiolato)tin(IV) in high yields. The reactions of bis(substituted 2-pyridyl) disulfides with tin(II) chloride proceeded in a similar way to give the corresponding dichlorodithiolatotin(IV) complexes. The results are given in Table 1.

Treatment of di-2-pyridyl disulfide *N*,*N'*-dioxide with tin(II) chloride or fluoride in an aqueous hydrohalogenic acid gives the complex of the dioxide with the tin(II) halide.[8] Dihalogenobis(2-pyridinethiolato *N*-oxide)-tin(IV) was prepared from 2-pyridinethiol *N*-oxide and tin(IV) halide.[7] In contrast, the treatment of di-2-pyridyl disulfide with tin(II) chloride in an aqueous hydrochloric acid afforded neither the tin(II) complex nor **1**, but 2(1*H*)-pyridinethione in 75% yield. No report seems to have appeared on such an oxidative addition of disulfide to tin(II) halide.[9]

The reaction was successfully extended to the preparation of other dihalogenodithiolatotin(IV) complexes. Dichlorobis(ethoxycarbonylmethanethiolato)tin(IV) was obtained from the reaction of bis(ethoxycarbonylmethyl) disulfide with tin(II) chloride in refluxing ethanol. The reaction of bis(dialkylthiocarbamoyl) disulfide with tin(II) chloride or fluoride in 1,2-dichloroethane afforded the corresponding dihalogenobis(dialkyldithiocarbamato)tin(IV), respectively. Since tin(II) halides are almost insoluble in 1,2-dichloroethane or benzene, the use of a soluble complex of tin(II) halide with an inert organic ligand such as triphenylphosphine oxide or hexahydro-2*H*-azepin-2-one was attempted with successful results. The advantage of this method lies in the fact that the reaction can be carried out smoothly in a homogeneous system affording a highly pure product in a good yield without purification process. Dichlorobis(2-pyridinethiolato *N*-oxide)-tin(IV) was prepared readily from the corresponding disulfide and the complex of tin(II) chloride with the ligand mentioned above. The results are given in Table 1.

Complex **1** can be obtained from the reaction of 2(1*H*)-pyridinethione with dichlorobis(organo-oxy)tin-(IV) such as bis(acetylacetonato)dichlorotin(IV).[2] It was also prepared either by the reaction of 2(1*H*)-pyridinethione with tin(IV) chloride in the presence of base, or by the treatment of tetrachlorobis[2(1*H*)-pyridinethione]tin(IV) with a large excess of water. The treatment of **1** with hydrogen chloride under anhydrous conditions afforded tetrachlorobis[2(1*H*)-pyridinethione]tin(IV). The results are illustrated in Scheme 1.

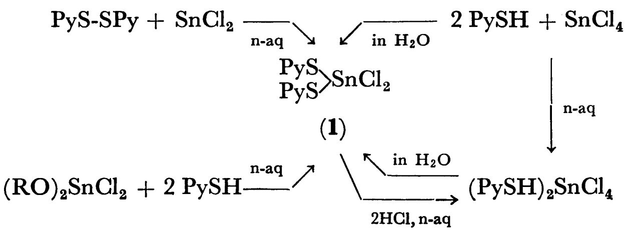
Table 1. Dichlorodithiolatotin(IV) [(RS)$_2$SnX$_2$]

Compound		Reaction conditions				Mp °C [lit]	Yield %	Anal, % Found (Calcd)				
R	X	Method[a]	Solvent	Temp	Time h			C	H	N	S	X
2-Pyridyl	Br	A	EDC	r. t.	5	278—280	81	24.30 (24.08)	1.69 (1.62)	5.62 (5.62)	12.78 (12.85)	
	I	A	EDC	r. t.	3	271—273	84	20.18 (20.26)	1.24 (1.36)	4.95 (4.73)	10.63 (10.82)	43.09 (42.81)
3-(CN)-4,6-Me$_2$-2-pyridyl	Cl	A	PhH	r. t.	1	259—260 (dec)	74	37.29 (37.24)	2.72 (2.73)	10.87 (10.86)	12.29 (12.43)	14.15 (13.74)
	Cl	C	PhH	r. t.	12		93					
3-(CN)-4-Me-6-Ph-2-pyridyl	Cl	A	PhH	r. t.	12	304—305 (dec)	88	49.40 (48.79)	2.93 (2.83)	8.72 (8.75)	10.12 (10.02)	10.87 (11.08)
	Cl	C	PhH	r. t.	12		90					
4,6-Me$_2$-2-pyridyl	Cl[b]	A	PhH	r. t.	12	198—201	55	36.06 (36.08)	3.40 (3.46)	6.19 ((6.01)	13.47 (13.76)	15.04 (15.22)
	Cl	C	Xylene[c]	refl.	2		90					
	Cl	B	PhH	refl.	2		57					
3-(CN)-6-Me-2-pyridyl	Cl	A	PhH	refl.	1	262—265 (dec)	78	34.79 (34.47)	2.13 (2.07)	11.95 (11.48)	13.38 (13.14)	14.30 (14.53)
	Cl	C	Xylene	refl.	1		97					
3-(COOEt)-6-Me-2-pyridyl	Cl	A	PhH (CCl$_4$)[d]	r. t.	2.5	165.5—166.0	84	37.20 (37.14)	3.37 (3.46)	4.96 (4.81)	11.04 (11.02)	12.37 (12.18)
3-(COOEt)-4,6-Me$_2$-2-pyridyl	Cl	C	PhH	refl.	1	202—203	84	39.25 (39.38)	3.71 (3.97)	4.52 (4.59)	10.45 (10.51)	11.62 (11.62)
5-(NO$_2$)-2-pyridyl	Cl	A	PhH (CCl$_4$-*i*-PrOH)[d]	r. t.	0.5	260—262 (dec)	67	24.33 (24.03)	1.30 (1.20)	11.38 (11.21)	13.07 (12.83)	14.14 (14.18)
1-Oxido-2-pyridyl	Cl	A	PhH	r. t.	3	300.5—302.0 (dec) [297—298.5][7]	94					
	Cl	C	PhH	70 °C	0.3		91					
2-Quinolyl	Cl	C	PhH	refl.	0.5	313—319 (dec)	97	42.51 (42.39)	2.29 (2.37)	5.60 (5.49)	12.84 (12.57)	14.14 (13.90)
4-Me-2-quinolyl	Cl	C	EDC	refl.	0.5	291—293 (dec)	87	44.45 (44.64)	2.93 (3.00)	5.46 (5.21)	11.83 (11.91)	13.06 (13.18)
Ethoxycarbonylmethyl	Cl	A	EtOH	r. t.	5	163—163.5	66	22.53 (22.45)	3.12 (3.30)		14.60 (14.99)	16.55 (16.57)
Dimethylthiocarbamoyl	Cl	A	EDC (PhH)[d]	r. t.	8.5	266—268 (dec) [244—246][3c]	94					
	F	A	EDC	refl.	6	300	90	18.64 (18.15)	3.19 (3.05)	7.25 (7.05)	32.54 (32.29)	
Diethylthiocarbamoyl	Cl	A	EDC	r. t.	48	211—212 [200—201][3c]	49					
	F[3b]	A	EDC (EtOAc)[d]	refl.	11	196—197 (dec)	70	26.70 (26.51)	4.39 (4.45)	6.21 (6.18)	28.31 (28.30)	
2-Benzothiazolyl	Cl	A	PhCH$_3$	refl.	7		trace[e]					

a) A and B indicate procedures similar to methods *a*) and *b*) for **1**, respectively, C indicates a procedure similar to the method reported for **1**.[2] b) Mol wt: Found: 481; Calcd: 466. c) refl.: refluxing temperature. d) The solvent in parentheses was used for separation of the products after termination of the reaction. e) The product could be confirmed only by mass spectrum; *m/e* 522(M$^+$).

Observation on Structure. Complex **1** is monomeric in dilute methyl isobutyl ketone (osmometry) at ambient temperature. The mass spectrum of **1** exhibits the monotin-containing, polyisotopic molecular ion (*m/e* 410) as the highest mass feature, which corresponds to the parent peak of the monomer. The remaining major peaks (*m/e* 375, 340, 300, 265, and 230) in the spectrum can be assigned to species resulting from the loss of one or two chlorine and/or a pyridinethiolato group from the parent molecular ion. However, no molecular ion corresponding to ditin-containing species was observed. This suggests that **1** is the monomeric tin(IV) complex.

The IR spectrum of **1** exhibits four bands due to



Py: pyridyl, n-aq: in non-aqueous organic solvent

Scheme 1.

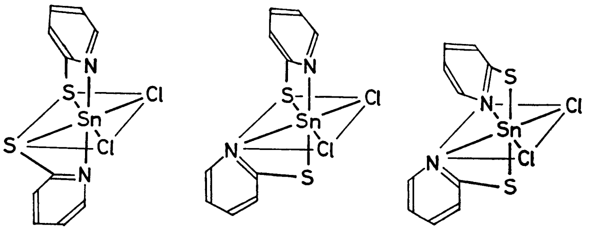


Fig. 1. Three possible structures for **1**. The enantiomers are possible for the respective structures.

ring vibration (C=C/C=N stretching) at 1580(s), 1550 (m), 1435(s), and 1420 cm^{-1}(s) in the 1600—1400 cm^{-1} region. This absorption pattern corresponds to that of di-2-pyridyl disulfide [1570(s), 1555(m), 1440(s), and 1410 cm^{-1} (s)], rather than to that of 2(1*H*)-pyridinethione [1610(m), 1575 (s; N-H bending), 1500(w), and 1435 cm^{-1} (m)]. The spectrum of **1** exhibits no remarkable band in C=S stretching spectral region, while a very strong intensity absorption band at 1136 cm^{-1} is observed in the spectrum of 2(1*H*)-pyridinethione. This indicates that the two 2-pyridinethiolato ligands in **1** exist not in an unequivocal thione form but rather in the thiol form like di-2-pyridyl disulfide. On the other hand, a difference in the spectra between **1** and di-2-pyridyl disulfide is observed in the absorption bands due to ring vibrations and C-H bending vibrations. The ring vibration frequencies which are present at 990 and 610 cm^{-1} in di-2-pyridyl disulfide shift to 1010 and 650 cm^{-1} in **1**, respectively. The shift to higher frequency region confirms the coordination of pyridine nucleus through nitrogen to tin atom.[10] The C-H out of plane bending vibration bands in **1** are at 770(m), 755(m), and 720 cm^{-1} (m), while the absorptions are at 750 (s; doublet) and 710 cm^{-1} (m) in the disulfide. The shift to higher frequency region in **1** can be interpreted again by the coordination of pyridine nucleus through nitrogen, which are likely to cause a depletion of π-electron density on the pyridine ring.[11] Additional information is available in the 500—200 cm^{-1} spectral region. Since a decisive assignment of all the bands in this region is difficult, dimethylbis(2-pyridinethiolato)tin(IV) was synthesized for comparison from dichlorodimethyltin(IV) and 2(1*H*)-pyridinethione. It was found that the three strong absorption bands at 310, 300, and 270 cm^{-1} are characteristic of **1**. The former two bands can be assigned to the Sn-Cl vibrations, since the frequency range is quite close to that of six-coordinated octahedral tin(VI) complexes[10,12-14] and absorption due to Sn-N vibration should be in a lower frequency region.[14] Two Sn-Cl stretching bands suggest *cis* configuration for the chlorine atoms in this complex, since only one Sn-Cl stretching band is expected for the *trans* configuration.[2,12]

Thus, six possible structures can be envisaged for **1**, *cis* Sn-S and *trans* Sn-N, *cis* Sn-S and *cis* Sn-N, and *trans* Sn-S and *cis* Sn-N, and their respective enantiomers. Three possible structures are shown in Fig. 1. However, it is not clear which structure is favorable, since no decisive information is available as to whether the two sulfur-tin bonds are *cis* or *trans*.

Consideration on Stability. Dihalogenobis(2-pyridinethiolato)tin(IV) is not sensitive to hydrolysis, being energetically so stable that it can be readily obtained under mild conditions from various starting materials including highly stable bis(acetylacetonato)dichlorotin(IV).[15] All the monomeric, octahedral dihalogenodithiolatotin(IV) complexes reported hitherto[3-7] are similarly stable. However, there has been no report on the dihalogenodithiolatotin(IV) complexes in which an intramolecular chelation is absent, except bis(benzenethiolato)dichlorotin(IV). Klages *et al.* reported that bis(benzenethiolato)dichlorotin(IV) can be obtained by the thermal dehydrochlorination of the complex prepared from 2 equiv of benzenethiol and tin(IV) chloride.[16]

In the course of repeated experiments on the reaction of benzenethiol with tin(IV) chloride in molar ratio 2 : 1 under several conditions, we could not isolate bis(benzenethiolato)dichlorotin(IV) but obtained diphenyl disulfide and tin(II) chloride together with tetrakis(benzenethiolato)tin(IV). This suggests that bis(benzenethiolato)dichlorotin(IV) is so unstable as to decompose giving diphenyl disulfide and tin(II) chloride or to disproportionate to tetrakis(benzenethiolato)-tin(IV) and tin(IV) chloride.

The stability of the dihalogenobis(2-pyridinethiolato)-tin(IV) could be ascribed to the octahedral structure with the four-membered chelate ring condensed with pyridine ring. In order to confirm this, syntheses of several dichlorodithiolatotin(IV) were attempted.

The reaction of bis(acetylacetonato)dichlorotin(IV) with 2(1*H*)-quinolinethione or 4-methyl-2(1*H*)-quinolinethione gave dichlorobis(2-quinolinethiolato)tin(IV) or its 4-methyl homolog as a stable complex in a good yield, as expected. Attempts to prepare dichlorotin(IV) derivatives of five-membered heterocyclethiol[17] were then made by reactions of bis(acetylacetonato)-dichlorotin(IV) or dichlorobis(hexahydro-2*H*-azepin-2-onato)tin(IV) with the various thiols or by reactions of tin(II) chloride with the corresponding disulfides. However, all the attempts were unsuccessful except for dichlorobis(2-benzothiazolethiolato)tin(IV), which could be obtained from either of the reactions as a very unstable product.

The unsuccessful syntheses can be ascribed to the unstability of the desired products. Dichlorotin(IV) derivative of the five-membered heterocyclethiols would not take an octahedral structure, since an intramolecular chelation would be hardly possible owing to the strain of four-membered chelate ring condensed with the five-membered cycle.[18] The unstability of a dichlorodi-

Table 2. Substituted dipyridyldisulfides [RSSR]

Compound	Solvent for recryst.	Mp °C	Yield %	Anal, % Found (Calcd) C	H	N	S
3-(CN)-4-Me-6-Ph-2-pyridyl	C_6H_6	200—201	97	69.46 (69.31)	3.70 (4.02)	12.65 (12.43)	14.16 (14.23)
4,6-Me_2-2-pyridyl	MeOH-H_2O	84.0—84.5	84	60.83 (60.83)	5.93 (5.83)	10.19 (10.13)	23.04 (23.20)
3-(COOEt)-6-Me-2-pyridyl	CCl_4	138—140	73	54.88 (55.08)	5.06 (5.14)	7.31 (7.14)	16.14 (16.34)
3-(CN)-6-Me-2-pyridyl	*i*-PrOH	172—173.5	68	56.47 (56.36)	3.43 (3.38)	18.29 (18.78)	21.99 (21.49)

thiolatotin(IV) which is not octahedral was also supported by an unsuccessful preparation of dichlorotin(IV) derivative of ethanethiol or phenylmethanethiol.

The results suggest that six-coordination with an intramolecular chelation is of considerable importance for stabilization of a monomeric dihalogenodithiolatotin(IV) complex.

Experimental

All the melting points were determined in a liquid bath and are uncorrected. The products were identified, unless otherwise stated, by comparison of the melting points and IR spectra with those of authentic samples as well as elemental analyses. The IR spectra were measured in KBr disk with a Hitachi Perkin-Elmer 225 Grating Infrared Spectrometer and a JASCO IR-G Grating Infrared Spectrometer. The molecular weight was determined in methyl isobutyl ketone with a Hitachi 115 Vapor Pressure Osmometer.

Materials. Commercial anhydrous $SnCl_2$ was used after drying over sulfuric acid. Substituted pyridyl disulfides were prepared from the corresponding substituted pyridinethiol by a procedure midified from that described for the preparation of di-2-pyridyl disulfides.[19] Appropriate thiol (0.1 mol) was dissolved in a solution of sodium ethoxide (0.1 mol) in ethanol (80—160 ml). To the resulting solution was added dropwise a solution of iodine (0.05 mol) in ethanol (90—190 ml). The precipitated product was collected and recrystallized. When the reaction mixture was homogeneous, it was concentrated under reduced pressure, and the residue was treated with water (120 ml) to give the crude disulfide, which was recrystallized. The results for new compounds are given in Table 2.

Dichlorobis(2-pyridinethiolato)tin(IV) ***1***. *a) Reaction of Di-2-pyridyl Disulfide with* $SnCl_2$: A solution of di-2-pyridyl disulfide (19.40 g, 88.1 mmol) in 1,2-dichloroethane (EDC, 70 ml) was added drop by drop to a suspension of $SnCl_2$ (13.76 g, 72.6 mmol) in EDC (50 ml) at 10 °C and the mixture was stirred at room temperature for 12 h. The precipitate was collected by filtration, washed with EDC(200 ml), and dried to give 28.86 g of a slightly pale yellow powdery solid; mp 275—277 °C (dec). The solid (6 g) was recrystallized from methyl isobutyl ketone (650 ml) to give slightly pale yellow prisms (4.33 g); mp 275—277 °C (dec). The product was identified with the specimen reported previously.[2] Yield, 97%. Mol wt: Found: 385; Calcd: 410.

The use of a solution of triphenylphosphine oxide–tin(II) chloride (41.22 g, 88.1 mmol) complex or hexahydro-2*H*-azepin-2-one–tin(II) chloride (36.64 g, 88.1 mmol) complex in EDC in place of the suspension of $SnCl_2$ gave a similar result.

*b) Treatment of Tetrachlorobis[2(1*H*)-pyridinethione]tin(IV) with Triethylenediamine*: A solution of trietylenediamine (2.81 g, 25 mmol) in benzene (30 ml) was added drop by drop to a suspension of tetrachlorobis[2(1*H*)-pyridinethione]tin(IV) (12.07 g, 25 mmol) in benzene (120 ml) at room temperature. After completion of the addition, the mixture was refluxed by heating for 2 h. The reaction mixture was filtered to give 14.69 g of a mixture of **1** and triethylenediamine dihydrochloride. The mixture was washed repeatedly with ice-water and then dried to give 10.04 g (98%) of **1**; mp 275—277 °C (dec).

*c) Treatment of Tetrachlorobis[2(1*H*)-pyridinethione]tin(IV) with Water*: Tetrachlorobis[2(1*H*)-pyridinethione]tin(IV) (4.83 g 10 mmol) was suspended in water (100 ml) and the mixture was stirred vigorously at room temperature for 20 min. The suspension was filtered, washed with water, and dried to give 3.45 g (84%) of **1**; mp 275—277 °C (dec).

Dichloro(triphenylphosphine oxide)tin(II). To a solution of triphenylphosphine oxide (5.56 g, 20 mmol) in benzene (40 ml) was added $SnCl_2$ (3.78 g, 20 mmol), and the mixture was heated with stirring to the refluxing temperature. The resulting solution was filtered and left to stand at room temperature under nitrogen atmosphere. The precipitated crystals were collected and washed with a small amount of benzene to give 9.92 g of dichloro(triphenylphosphine oxide)tin(II)–benzene adduct (1 : 1) as colorless crystals; mp 81—84 °C (sinter at 67 °C). Found: C, 52.97; H, 3.89; Cl, 12.91%. Calcd for $C_{30}H_{26}Cl_2OPSn$; C, 52.89; H, 3.70; Cl, 13.01%.

The adduct was dried at 50 °C under reduced pressure to give the benzene free adduct; mp 96—97 °C.

Found: C, 46.13; H, 3.37; Cl, 15.14%. Calcd for $C_{24}H_{20}Cl_2OPSn$: C, 46.16; H, 3.21; Cl, 15.18%.

4,6-Dimethyl-2-pyridinethiol. A suspension of 3-cyano-4,6-dimethyl-2-pyridinethiol[20] (48.21 g, 294 mmol) in 250 ml of aqueous hydrobromic acid (48%) was heated with refluxing for 4 h and left to stand at room temperature for several hours. The resulting precipitate was filtered and recrystallized from ethanol (1700 ml) to give 9.31 g (17%) of 2-mercapto-4,6-dimethyl-3-pyridinecarboxylic acid; mp 253—254 °C (dec). Found: C, 52.40; H, 4.99; N, 7.57; S, 17.70%. Calcd for $C_8H_9NO_2S$: C, 52.44; H, 4.95; N, 7.64; S, 17.50%.

The filtrate separated from the carboxylic acid was diluted with water (1500 ml) and allowed to stand overnight at room temperature to give 11.64 g of yellow precipitate. Recrystallization from acetonitrile (800 ml) gave 7.50 g (18%) of the title compound as yellow prisms; mp 239—241 °C. Found: C, 60.42; H, 6.52; N, 10.18; S, 22.74%. Calcd for C_7H_9NS: C, 60.39; H, 6.52; N, 10.06; S, 23.03%.

Ethyl 2-Mercapto-6-methyl-3-pyridinecarboxylate. Into a suspension of 2-mercapto-6-methyl-3-pyridinecarboxylic acid[21] (14.44 g, 85.3 mmol) and ethanol (200 ml) was passed dry hydrogen chloride with refluxing by heating for

5 h and the mixture was allowed to stand at room temperature overnight. The resulting crystalline precipitate was collected (9.60 g) and neutrallized by treating with an aqueous solution of sodium hydrogen carbonate. Recrystallization from diisopropyl ether (1500 ml) gave 5.41 g (32%) of yellowish prisms; mp 129—131 °C. Found: C, 54.69; H, 5.40; N, 7.11; S, 16.23%. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10; S, 16.22%.

Ethyl 2-Mercapto-4,6-dimethyl-3-pyridinecarboxylate. Into a homogeneous mixture of ethyl cyanoacetate (80 g, 0.7 mol), pyridine (80 ml) and triethylamine (50 ml) was passed dry hydrogen sulfide at room temperature for 7 h. The reaction mixture was poured into water (250 ml) and extracted three times with diisopropyl ether. The combined extracts were concentrated and the residue was chromatographed on a silica gel (Wakogel C-200) column, immersed in benzene. Elution with benzene-1-butanol (4 :1) afforded ethyl thiocarbamoylacetate (55.33 g) as the first running substance. A mixture of the thiocarbamoylacetate (40.22 g, 0.27 mol), acetylacetone (54.7 g, 0.55 mol) and triethylamine (10 g) was heated at 50 °C for 5 h, and then treated with diisopropyl ether (100 ml). The crystalline product was recrystallized twice from isopropyl alcohol (350 ml)–diisopropyl ether (150 ml) to give 35 g (61%) of pale brown needles; mp 154.5—155.5 °C. Found: C, 57.05; H, 6.25; N, 6.76; S, 15.00%. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.17%.

*Reaction of **1** with Hydrogen Chloride.* Into a suspension of **1** (4.10 g, 10 mmol) in EDC (100 ml) was passed dry hydrogen chloride (400 ml) below −20 °C. The reaction mixture was concentrated under reduced pressure, and the residue was treated with EDC (100 ml). Filtration followed by drying at 100 °C under reduced pressure for 5 h gave 4.83 g (100%) of tetrachlorobis[2(1*H*)-pyridinethione]tin(IV), which was identified with the authentic specimen described below.

*Tetrachlorobis[2(1*H*)-pyridinethione]tin(IV).* A solution of tin(IV) chloride (3.13 g, 12 mmol) in EDC (20 ml) was added drop by drop to a solution of 2(1*H*)-pyridinethione (2.67 g, 24 mmol) in EDC (80 ml) with stirring at room temperature. After the addition, the mixture was stirred for 15 h. The resulting solid was collected by filtration, washed with EDC (30 ml), and dried to give 5.79 g (100%) of yellow crystalline powder; mp 224—226 °C. Found: C, 25.22; H, 2.12; N, 6.11; S, 13.34; Cl, 29.10%. Calcd for $C_{10}H_{10}Cl_4N_2S_2Sn$: C, 24.87; H, 2.09; N, 5.80; S, 13.28; Cl, 29.37%.

Dimethylbis(2-pyridinethiolato)tin(IV). To a solution of sodium ethoxide (30.4 mmol) in ethanol (150 ml) was added 2(1*H*)-pyridinethione (3.38 g, 30.4 mmol) and then dimethyldichlorotin(IV) (1.82 g, 15.2 mmol). After being stirred at room temperature for 2 h, the mixture was concentrated and the residue was treated with water (200 ml). The insoluble substance was collected by filtration, washed with water (30 ml) and dried to give 2.96 g of crude product, which was recrystallized from isopropyl alcohol (40 ml) to give 2.62 g (47%) of colorless needles; mp 139 °C. IR (KBr): 1570, 1550, 1445, 1410, 990, 740, 720, 620, 395, and 360 cm^{-1}. Found: C, 39.00; H, 3.77; N, 7.39; S, 17.41%. Calcd for $C_{12}H_{14}N_2S_2Sn$: C, 39.05; H, 3.82; N, 7.59; S, 17.38%.

An Attempted Synthesis of Bis(benzenethiolato)dichlorotin(IV). A solution of bis(benzenethiol)tetrachlorotin(IV),[16] prepared by adding a solution of tin(IV) chloride (10.42 g, 40 mmol) in EDC (50 ml) to a solution of benzenethiol (8.82 g, 80 mmol) in EDC (100 ml) below −20 °C, was refluxed by heating for 8 h, during which dry nitrogen gas was passed through a capillary in the mixture, in order to remove hydrogen chloride formed. Eighty percent of hydrogen chloride based on benzenethiol was trapped in 0.5 M aqueous sodium hydroxide solution from the exhaust nitrogen gas. The product precipitated in the reaction mixture was collected by filtration and confirmed to be $SnCl_2$ (1.20 g, 16% based on $SnCl_4$) by being converted into dichloro(triphenylphosphine oxide)tin(II), which was identified with the authentic sample. To the filtrate was added triphenylphosphine oxide (9.39 g, 33.7 mmol), and the mixture was stirred for 0.5 h. The mixture was then concentrated and the residue was treated with benzene (150 ml). The resulting precipitate was collected by filtration, washed with benzene (70 ml), and dried to give 13.72 g (42% based on $SnCl_4$ used) of tetrachlorobis(triphenylphosphine oxide)tin(IV); mp 330—332 °C (lit,[22] mp 323 °C). The filtrate separated from the tin(IV) complex and the washing were combined and concentrated, and to the residue was added hexane (30 ml). The insoluble yellow crystals were collected by filtration and washed with hexane (15 ml × 2). Crude tetrakis(benzenethiolato)tin(IV) (**2**) was obtained: 6.40 g. The combined filtrate and washings were concentrated and the residue was chromatographed on a silica gel column (Wakogel C-300) immersed in hexane. Elution with hexane afforded 1.35 g (7.7% based on benzenethiol) of diphenyl disulfide; mp 58—60 °C (lit,[23] mp 60—62 °C). Subsequent elution with benzene gave 1.26 g of **2**, which was identified by its IR spectrum. Two crops of **2** were combined and recrystallized from isopropyl alcohol (220 ml). Pale yellow needles, 4.06 g (18% based on $SnCl_4$); mp 65—66.5 °C (lit,[24] 63—64 °C).

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