Syntheses and Spectral Observation on the Structure of Several 2(1*H*)-Pyridinethionato Zinc Complexes

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(Received June 28, 1978)

Although bis[2(1*H*)-pyridinethionato]zinc (**1**) is prepared by the reaction of 2(1*H*)-pyridinethione with zinc chloride in the presence of stoichiometric amount of sodium hydroxide, a similar reaction in the presence of a large excess amount of the base gave μ_4-oxo-hexakis-μ-[2(1*H*)-pyridinethionato-(*N,S*)]-tetrazinc (**2**) which is the first example of L_6Zn_4O (L=ligand) type complexes having heterocyclic thiolato groups as ligands. The complex **2** was also prepared by several routes, which involve hydrolysis of **1** and the reaction of **1** with zinc oxide. In these complexes 2(1*H*)-pyridinethionato ligand acts as a bidentate or bridging ligand. Attempts to convert bis(4,6-dimethyl-2-pyridylthio)zinc or bis(1-oxido-2-pyridylthio)zinc into a complex of L_6Zn_4O type were failed. Complexes of L_6Zn_4O type were also prepared when L were 2-thiazolidinethionato, 5-methyl-2-thiazolidinethionato, and 1-methyl-4-imidazoline-2-thionato.

In the previous papers,[1,2] the synthesis and the molecular structure of dichlorobis[2(1*H*)-pyridinethionato]tin(IV) were reported. The 2(1*H*)-pyridinethionato ligands act as bidentate ligands in the complex, which has an octahedral structure resulted from the intra-molecular four-membered (Sn, S, C, and N) chelate rings formation.

Several metal (Ru,[3,4] Ir,[5] Fe,[6] Rh,[7] Hg[8]) derivatives of 2(1*H*)-pyridinethione have been reported. The 2-pyridylthio group acts as a bidentate,[3,5] unidentate,[6-8] or bridging ligand.[4]

We have studied zinc derivatives of 2(1*H*)-pyridinethione. This paper deals with the transformation of bis[2(1*H*)-pyridinethionato]zinc (**1**) into a new zinc complex, μ_4-oxo-hexakis-μ-[2(1*H*)-pyridinethionato-(*N,S*)]-tetrazinc (**2**) and an observation on the coordination of 2(1*H*)-pyridinethionato ligand in **1** and **2**. This paper also describes syntheses of several new zinc derivatives of heterocyclic thiols.

Results and Discussion

Syntheses. Bis[2(1*H*)-pyridinethionato]zinc (**1**) is briefly reported in a patent,[9] but no characterization of **1** is described. The zinc derivative **1** was obtained as a sole product when the molar ratio of the three reactants was stoichiometric (2: 1: 2), as shown in Eq. 1.

$$\mathrm{2PySH + ZnCl_2 + 2NaOH \longrightarrow (PyS)_2Zn + 2NaCl + 2H_2O} \qquad (1)$$

$$\mathrm{8PySH + 4ZnCl_2 + 10NaOH \longrightarrow (PyS)_6Zn_4O + 8NaCl + 2PySNa + 9H_2O} \qquad (2)$$

When the reaction was performed in the presence of a large excess amount of sodium hydroxide, a new complex μ_4-oxo-hexakis-μ-[2(1*H*)-pyridinethionato-(*N,S*)]-tetrazinc (**2**) was found to be formed according to Eq. 2.

The complex **2** was best prepared by the reaction in a molar ratio of 3: 2: 4 as shown in Scheme 1. The composition of **2** was determined by elemental analyses, alternative synthetic reactions, and the reaction with 2(1*H*)-pyridinethione giving again **1**. The complex **2** was alternatively prepared by several routes as shown in Scheme 1.

$$\mathrm{6PySH + 4ZnCl_2 + 8NaOH} \xrightarrow{-8\mathrm{NaCl},\ -7\mathrm{H_2O}} \mathbf{2}$$

$$4\,\mathbf{1} + \mathrm{H_2O} \xrightleftharpoons{-2\mathrm{PySH}} \mathbf{2}$$

$$3\,\mathbf{1} + \mathrm{ZnO} \longrightarrow \mathbf{2}$$

$$\mathrm{6PySH + 4ZnO} \xrightarrow{-3\mathrm{H_2O}} \mathbf{2}$$

Scheme 1. Syntheses of μ_4-oxo-hexakis-μ-[2(1*H*)-pyridinethionato-(*N,S*)]-tetrazinc (**2**).

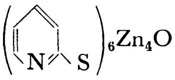
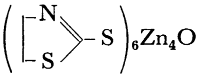
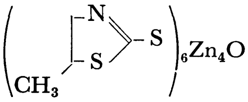
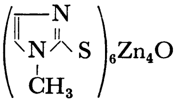
When a suspension of **1** in water was refluxed for 1 h, **2** was obtained as an insoluble product and 2(1*H*)-pyridinethione was recovered from the aqueous solution in a quantitative yield based on the equation shown in Scheme 1. A treatment of **1** with zinc oxide in a molar ratio of 3: 1 in refluxing acetonitrile also gave **2**. A reaction of 2(1*H*)-pyridinethione and zinc oxide in a molar ratio of 3: 2 in 1,2-dichloroethane yielded **2**. In contrast, complex **1** was obtained by the reaction of the same reagents in a molar ratio of 2: 1 in boiling benzene with azeotropical removal of water formed.[10]

When **2** was treated with twice molar amount of 2(1*H*)-pyridinethione in boiling benzene under azeotropical removal of water produced, **1** was again obtained in a quantitative yield.

Bis(4,6-dimethyl-2-pyridylthio)zinc (**3**) was prepared from 4,6-dimethyl-2(1*H*)-pyridinethione by a reaction similar to Eq. 1 and by a reaction of bis(4,6-dimethyl-2-pyridyl) disulfide with zinc dust.[11] Transformations of **3** and bis(1-oxido-2-pyridylthio)zinc into the complexes of L_6Zn_4O (L=ligand) type were attempted by heating L_2Zn compounds in water, but the major amount of starting materials was recovered, and the expected complexes could not be obtained.

Although a large number of bis(organo ligand)zinc are known, there have been reported only four types of L_6Zn_4O complex formed with alkanecarboxylato,[12] *O,O*-dialkyl(or diaryl)phosphorodithioato,[13] dialkylphosphinothioato,[14] and 1,3-diphenyltriazenato.[15] The complex **2** is the first example of oxotetrazinc complex, where the ligand is a heterocyclic thiolato group. Syntheses of several other complexes of L_6Zn_4O type where L is a heterocyclic thiolato group were examined. Complexes of L_6Zn_4O type were synthesized by the re-

Table 1. Hexakis-μ-(heterocyclic thiolato)-μ_4-oxo-tetrazinc

Product	Mp	IR (cm^{-1})	Found Calcd (%)			
			C	H	N	S
 **2**	above 340 °C (dec)[25]	1590s, 1545m, 1455s, 1410s, 1270m, 1155m, 1135s(sh), 1130s, 1085m, 1050m, 1010m, 775m, 765m, 755m, 725m, 645w, 540m, 530m, 515m, 495w, 445w, 415w, 360w, 265m(br)	38.61 38.40	2.47 2.58	8.74 8.96	20.33 20.50
	above 170 °C (dec)	1500s, 1450w, 1310m, 1200w, 1040s, 980s, 940m, 510m (br), 435w, 325w	22.01 21.91	2.41 2.45	8.43 8.52	38.85 38.99
	175—220 °C(dec) [EtOH]	1505s, 1440m, 1375m, 1305m, 1195m, 1025s, 1005s (sh), 920m, 510m (br), 460w (sh), 385w, 350w, 305w	27.09 26.91	3.29 3.39	7.64 7.85	36.15 35.92
 **8**	above 255 °C (dec)	1535w, 1455s, 1415m, 1370s, 1315m, 1285m, 1145s, 735m (br), 690s, 515m (br), 315w, 220m (br)	29.92 30.14	2.89 3.16	17.65 17.57	20.33 20.11

action of 2-thiazolidinethione (**4**), 5-methyl-2-thiazolidinethione (**5**), 1-methyl-4-imidazoline-2-thione (**6**) with zinc chloride in the presence of sodium hydroxide (molar ratio of 3: 2: 4) in an aqueous solution. The results are shown in Table 1. However, L_2Zn derivatives of these five membered heterocyclic thiols could not be prepared by the reaction of the thiols with zinc chloride in the molar ratio of 2: 1. Bis(1-methyl-4-imidazoline-2-thionato)zinc (**7**) could be prepared only by the reaction of hexakis-μ-(1-methyl-4-imidazoline-2-thionato)-μ_4-oxo-tetrazinc (**8**) with the thione **6**. Attempts to prepare L_2Zn derivatives of **4** and **5** were unsuccessful by analogous reactions from the corresponding L_6Zn_4O type complexes.

Observation on Structure. The MS spectrum (double focus) of **1** exhibits a very weak dizinc-containing polyisotopic molecular ion (*m*/*e* 568) as the highest mass feature, which corresponds to the parent peak of the dimer. Three dizinc-containing molecular ions observed at *m*/*e* 490 (M—Py), 458 (major peak, M—PyS), 426 (M—PyS—S) seem to be fragments derived from the dimer, and a monozinc-containing molecular ion at *m*/*e* 316 [$(PyS)_2ZnS$] is also indicative for dimeric structure of **1**. Molecular weight measurement (osmometry) showed that **1** was dimeric in 4-methyl-2-pentanone.[16]

The IR spectrum of **1** exhibits bands due to ring vibration at 1595 (s), 1545 (s), 1455 (s, doublet), 1420 (s, doublet), 1020 (m), 645 cm^{-1} (w), and the bands due to C–H bending vibration at 765(sh) and 755 cm^{-1} (s).[1,17] The bands at 1020 and 645 cm^{-1} have shoulders. The absorption pattern is close to that of dichlorobis[2(1*H*)-pyridinethionato] tin(IV).[18] This fact suggests that 2(1*H*)-pyridinethionato ligands act as bidentate ligands. These bands all shifted in higher frequency region in comparison with the corresponding bands of di-2-pyridyl disulfide.[1] The shift can be interpreted by the coordination of pyridine nucleus through nitrogen to tin atom. A strong intensity absorption band appears at 1135 cm^{-1} in the spectrum of **1**, which can be assigned to C=S stretching since 2(1*H*)-pyridinethione shows the strong absorption of C=S stretching at the same position.[19] This band indicates the presence of 2(1*H*)-pyridinethionato ligand of thione form, whose coordination to zinc through sulfur atom is weak as in the iridium complex.[5] Based on these spectral data 2(1*H*)-pyridinethionato ligands act as bidentate or bridging one and **1** seems not monomeric.

Molecular weight of **2** could not be determined owing to the low solubility to the ordinary solvent for osmometric measurement. The MS spectrum (chemical ionization with isobutane) of **2** exhibits the zinc-containing, polyisotopic molecular ion (*m*/*e* 839) as the highest mass feature which corresponds to species resulting from loss of one pyridyl group and one oxygen atom from [M+H]. The remaining major peaks (*m*/*e* 743, 568, 459) in the spectrum can be assigned to species resulting from loss of one or more 2(1*H*)-pyridinethionato groups, zinc atoms, and oxygen atom from [M+H] or [M].

The IR absorption pattern of **2** in the region higher than 600 cm^{-1} is very close to that of **1**, except that the bands at 1455, 1410, 1010, and 645 cm^{-1} in **2** are all single peaks. This fact seems to suggest that six 2(1*H*)-pyridinethionato ligands in **2** are in chemically similar states. The characteristic absorption band of **2** is a broad triplet with medium intensity, whose peaks are at 540, 530, and 515 cm^{-1}. The broad and strong intensity absorption bands of zinc oxide in the 540—400 cm^{-1} spectral region were replaced with the triplet bands, when zinc oxide was allowed to react with **1** to give **2**. The triplet bands can be ascribed to Zn–O bond, since the absorptions of zinc–sulfur vibrations have been described to appear in the region lower than 401 cm^{-1} in several compounds containing Zn–S bond,[20] and the absorptions due to Zn–N bond are found between 250 and 200 cm^{-1} in complexes of pyridine compound with zinc halides.[21] The band at 526 cm^{-1} in hexa-μ-acetato-(*O*,*O*′)-μ_4-oxo-tetrazinc has been assigned to $\nu(Zn_4O)$.[22]

The structures of L_6Zn_4O complexes where L is AcO, $(BuO)_2PS_2$, or Ph_2N_3 have been determined by X-ray analyses.[12a,13a,15] The replacement of –O–C–O–, –S–P–S–, or –N–N–N– moiety in the structures of those complexes with –S–C–N– moiety gives a possible structure for **2** as shown in Fig. 1. The IR spectral observation mentioned above supports the structure for **2**.

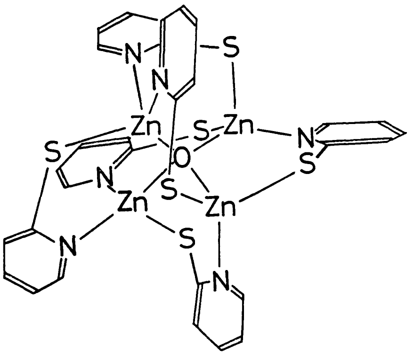


Fig. 1. A possible structure for **2**.

The transformation of **1** into **2** can be explained by the substitution of one 2(1*H*)-pyridinethionato ligand in the dimer of **1** with oxygen of water or zinc oxide and the simultaneous or subsequent coupling of two $(PyS)_3Zn_2$ group through the oxygen, as shown in Eq. 3 or 4.

$$2(PyS)_3Zn_2(SPy) + H_2O \longrightarrow [(PyS)_3Zn_2]_2O + 2HSPy \tag{3}$$

$$2(PyS)_3Zn_2(SPy) + ZnO \longrightarrow [(PyS)_3Zn_2]_2O + Zn(SPy)_2 \tag{4}$$

$$[2Zn(SPy)_2 \longrightarrow (PyS)_3Zn_2(SPy)]$$

Bis(4,6-dimethyl-2-pyridylthio)zinc (**3**) is monomeric based on the molecular weight (osmometry) and MS spectrum. No remarkable difference is observed in the IR spectrum of C=C/C=N stretching region and C=S stretching region between **3** and bis(4,6-dimethyl-2-pyridyl) disulfide. Furthermore, there was not recognized such a shift of bands due to ring vibration and C–H bending vibration as observed between **1** and the corresponding disulfide. These data show that **3** is a simple zinc salt of a thiol and no such strong coordination of pyridine ring through nitrogen on metal is observed as in the case of **1**. This may be a reason why **3** could not be converted to a complex of L_6Zn_4O type.

Experimental

All the melting points were determined in a liquid bath placing a cut edge of capillary outside of the bath, and were uncorrected. The IR spectra were measured with a Hitachi Perkin-Elmer 225 and a Hitachi EPI-G2 Grating Infrared Spectrometer. The molecular weight was determined in 4-methyl-2-pentanone with a Hitachi 115 Vapor Pressure Osmometer. The MS spectra were measured with a Hitachi M60 Mass Spectrometer equipped with computer system 002B, a Hitachi M52 Mass Spectrometer, or a JMS-01SG-2 Double Focus Mass Spectrometer.

Materials. Commercial anhydrous zinc chloride was used after drying over phosphorus pentaoxide. Commercial 2(1*H*)-pyridinethione, 2-thiazolidinethione (**4**), and 1-methyl-4-imidazoline-2-thione (**6**) were used after recrystallization. 5-Methyl-2-thiazolidinethione (**5**) was prepared by the procedure previously reported.[23]

*Bis[2(1H)-pyridinethionato]zinc (**1**).* *a) Reaction of 2(1H)-Pyridinethione with Zinc Chloride in the Presence of Base:* To an aqueous solution of sodium hydroxide (1/2 M, 20 ml) was added 2(1*H*)-pyridinethione (1.11 g, 10 mmol). To the resulting solution was added drop by drop a solution of zinc chloride (95%, 0.72 g, 5 mmol) in water (15 ml) with stirring at 20 °C and the mixture was stirred at 20 °C for 2 h. The resulting slightly yellowish precipitate was filtered and washed with water (50 ml) to give 1.41 g (99%) of **1**; mp 248—251 °C.[24] Mol wt, Found: 603; Calcd (dimer): 571. Found: C, 42.07; H, 2.75; N, 9.68; S, 22.46%. Calcd for $C_{10}H_8N_2S_2Zn$: C, 42.04; H, 2.82; N, 9.81; S, 22.45%.

b) Reaction of 2(1H)-Pyridinethione with Zinc Oxide: To a suspension of zinc oxide (0.81 g, 10 mmol) in benzene (150 ml) was added 2(1*H*)-pyridinethione (2.44 g, 22 mol). A mixture was stirred at room temperature for 1 h and then refluxed for 5 h, during which boiling benzene was gradually distilled out to remove water azeotropically, while dried benzene was supplied to the mixture at intervals. The precipitate was collected by filtration and washed with benzene (60 ml) to give 2.73 g (96%) of slightly yellowish powder. The IR spectrum of the powder was identical with that of **1**.

*μ_4-Oxo-hexakis-μ-[2(1H)-pyridinethionato-(N,S)]tetrazinc (**2**).* *a) Reaction of 2(1H)-Pyridinethione with Zinc Salt in the Presence of Base in Water:* A solution of zinc chloride (95%, 0.72 g, 5 mmol) in water (30 ml) was added drop by drop to a solution of 2(1*H*)-pyridinethione (0.83 g, 7.5 mmol) in 1/2 M aqueous sodium hydroxide (20 ml) with stirring at room temperature. After stirring the mixture at room temperature for 22 h, the precipitate was collected by filtration and washed with water (50 ml) to give 1.12 g (96%) of colorless crystalline powder: mp above 340 °C (gradually dec).[25] MS (CI): *m/e* 839 $[(PyS)_5Zn_4SH]$, 820 $[(PyS)_5(Py)Zn_3]$, 743 $[(PyS)_5Zn_3H]$, 727 $[(PyS)_4(Py)Zn_3OH]$, 664 $[(PyS)_4Zn_3S]$, 632 $[(PyS)_4Zn_3]$, 608, 568 $[(PyS)_4Zn_2]$, 554 $[(PyS)_3Zn_3S]$, 536 $[(PyS)_3(Py)Zn_2]$, 491 $[(PyS)_3Zn_2SH]$, and 459 $[(PyS)_3Zn_2H]$.

*b) Hydrolysis of **1**:* A suspension of **1** (10.0 g, 35 mmol) in water (200 ml) was refluxed for 1 h. The precipitate was collected by filtration and washed with water (50 ml) to give 8.13 g (99%) of colorless crystalline powder. The IR spectrum of the solid was identical with that of **2**. The filtrate separated from **2** and washings were combined and concentrated under reduced pressure. The residue was extracted with acetone (100 ml). The acetone extract was concentrated under reduced pressure to give 1.95 g (100%) of 2(1*H*)-pyridinethione as yellow crystals; mp 124—126 °C (lit, mp 125 °C[26]). When **1** was treated in boiling water for 28 h, the same product was obtained without further decomposition. Found: C, 38.48; H, 2.66; N, 8.96; S, 20.25; Zn, 27.43%. Calcd: Zn, 27.87%.

*c) Reaction of **1** with Zinc Oxide:* A mixture of **1** (4.29 g, 15 mmol) and zinc oxide (0.41 g, 5 mmol) in acetonitrile (100 ml) was refluxed for 4 h. The precipitate was collected by filtration and washed with acetonitrile (40 ml) to give 4.54 g (97%) of colorless crystalline powder. The IR spectrum of the solid was identical with that of **2**.

d) Reaction of 2(1H)-Pyridinethione with Zinc Oxide: Zinc oxide (1.63 g, 20 mmol) was added to a solution of 2(1*H*)-pyridinethione (3.34 g, 30 mmol) in 1,2-dichloroethane (100 ml) and the mixture was stirred at room temperature for 5 h. The precipitate was collected by filtration and washed with 1,2-dichloroethane (40 ml) to give 4.41 g (94%) of crystalline powder. The IR spectrum of the solid was identical with that of **2**.

Reaction of **2** *with 2(1*H*)-Pyridinethione.* To a solution of 2(1*H*)-Pyridinethione (0.53 g, 4.8 mmol) in benzene (100 ml) was added **2** (1.88 g, 2 mmol) and the mixture was refluxed for 5 h, during which boiling benzene was gradually distilled out in order to remove water azeotropically, while dried benzene was supplied to the mixture at intervals. The precipitate was collected by filtration and washed with benzene (50 ml) to give 2.22 g (97%) of slightly yellowish solid. The IR spectrum of the solid was essentially identical with that of **1**.

Bis(4,6-dimethyl-2-pyridylthio)zinc (**3**). *a) Reaction of 4,6-Dimethyl-2(1*H*)-pyridinethione with Zinc Chloride in the Presence of Base*: To an aqueous solution of sodium hydroxide (1/2 M, 4.6 ml) was added 4,6-dimethyl-2(1*H*)-pyridinethione 0.28 g, 2 mmol). To the resulting solution was added drop by drop a solution of zinc chloride (95%, 0.14 g, 1 mmol) in water (20 ml) with stirring at 20 °C and the mixture was stirred for 2.5 h. The precipitate was collected by filtration and washed with water to give 0.29 g of colorless solid. The solid was recrystallized from 90 ml of ethanol to give 0.10 g (29%) of prisms; mp 250—252 °C (dec). IR (KBr): 1595s, 1545 s, 1450 m, 1395 m, 1370 m, 1275 m, 1205 m, 1135 m, 875 m, 840 m, 825 m, 535 w, 530 m, 430 w, 270 w(br), and 235 m(br) cm^{-1}. Mol wt, Found: 364; Calcd (monomer): 342. MS(EI): *m/e* 340 (M), 325, 307, and 202. Found: C, 49.15; H, 4.65; N, 8.24; S, 18.81%. Calcd for $C_{14}H_{16}N_2S_2Zn$: C, 49.20; H, 4.72; N, 8.20; S, 18.76%.

b) Reaction of Bis(4,6-dimethyl-2-pyridyl) Disulfide with Zinc Dust: A mixture of bis(4,6-dimethyl-2-pyridyl)disulfide (5.00 g, 18 mmol) and zinc dust (1.18 g, 18 mg atom) in benzene (100 ml) was refluxed for 26 h. The reaction mixture was filtered to give 4.53 g of a mixture of white powdery solid and zinc dust, which was extracted by Soxhlet's extractor with benzene for 10 h. Colorless crystals were obtained from the extract. Yield 3.08 g (50%); mp 251—252 °C (dec). The IR spectrum of the crystals was identical with that of **3** obtained in a).

Bis(1-methyl-4-imidazoline-2-thionato)zinc (**7**). A mixture of hexakis-μ-(1-methyl-4-imidazoline-2-thionato)-μ_4-oxotetrazinc (**8**) (0.96 g, 1 mmol) and 1-methyl-4-imidazoline-2-thione (**6**) (0.46 g, 4 mmol) in benzene (100 ml) was refluxed for 15 h, during which benzene was gradually distilled out in order to remove water azeotropically, while dried benzene was supplied to the mixture at intervals. The precipitate was collected by filtration and washed with benzene (50 ml) to give 1.11 g of colorless solid. The solid (0.48 g) was added again to a solution of **6** (0.46 g, 4 mmol) in benzene (200 ml). The mixture was refluxed for 2.5 h, during which benzene was distilled out and supplied in the same manner mentioned above. The precipitate was collected by filtration and washed with benzene (50 ml) to give 0.44 g of colorless solid; mp above 300 °C (gradually dec). IR (KBr): 1575w, 1535m, 1455s, 1410m, 1370s, 1315m, 1285s, 1145s, 1085w, 955m, 725m (br), 690s, 510m, 435w, 315w, and 250w cm^{-1}. MS(CI): *m/e* 853 $[(LS)_5Zn_4S]$ (LSH=**6**), 837 $[(LS)_5LZn_3\text{-}H]$, 547 $[(LS)_3LZn_2\text{-}H]$, 467 $[(LS)_3Zn_2]$, 403 $[(LS)L_2Zn_2]$, 331, 291 $[(LS)_2ZnH]$, and 115 $[LSH_2]$. Found: C, 33.16; H, 3.25; N, 19.26; S, 21.84%. Calcd for $C_8H_{10}N_4S_2Zn$: C, 32.94; H, 3.46; N, 19.26; S, 21.98%.

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16) A referee pointed out a possibility that **1** may be polymeric and dissociates into dimeric form in 4-methyl-2-pentanone. Although a higher association of the dimer is possible in crystalline state, the dimeric form seems to be a basic unit for bis[2(1*H*)-pyridinethionato]zinc based on not only MS data of crystals and osmometric molecular weight determination, but also the reaction of **2** with benzoyl chloride giving chlorotris[2(1*H*)-pyridinethionato]dizinc and benzoylthiopyridine: S. Matsunami, S. Fujimura, K. Okimoto, and M. Masaki, submitted for publication to *Bull. Chem. Soc. Jpn.*

17) In a previous report,[1] we assigned the band at 710 or 720 cm^{-1} in di-2-pyridyl disulfide or 2(1*H*)pyridinethionatotin(IV) complex to a C–H bending vibration based on literatures: S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964); H. Shindo and N. Ikekawa, *Chem. Pharm. Bull.*, **4**, 192 (1965). However, it seems to be more probable to assign these bands to C–C ring deformations: N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, **19**, 2197 (1966). Complexes **1** and **2** also exhibit medium intensity bands at 725 cm^{-1} assignable to the C–C ring deformation. The shift of the bands to higher frequency region compared with that of di-2-pyridyl disulfide seems also to indicate the coordination of pyridine nucleus to zinc.

18) The bands corresponding to those bands at 1455, 1420, 1020, and 645 cm^{-1} in **1** are singlets in the spectrum of dichlorobis[2(1*H*)-pyridinethionato]tin(IV).

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24) In our previous description, we recorded for **1** the value of 240 °C, at which this compound began to decompose: M. Masaki, S. Matsunami, K. Okimoto, and S. Fujimura, Japan Kokai 88970 (1976); *Chem. Abstr.*, **85**, 178503j (1976). The value was obtained by a measurement which was done by setting a capillary in a sulfuric acid bath. The sample might be exposed to the vapor of sulfuric acid, which could be introduced from a cut edge of the capillary placed inside of the bath.

25) In the measurement of mp, it was observed that the product began coloring gradually at about 340 °C and decomposed and melted at 380—385 °C.

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