Syntheses of Chlorozinc Complexes of 2(1*H*)-Pyridinethione and Their Mutual Transformations

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Three types of zinc complexes, chlorotris[2(1*H*)-pyridinethionato]dizinc (**3**), dichlorotetrakis[2(1*H*)-pyridinethionato]trizinc (**4**), and chloro[2(1*H*)-pyridinethionato]zinc (**5**) were produced by the reactions of bis[2(1*H*)-pyridinethionato]zinc (**2**) and zinc chloride. The product in the reactions varies depending on the solvent. The mutual transformation reactions among **3**, **4**, **5**, **2**, and oxohexakis[2(1*H*)-pyridinethionato]tetrazinc were described. The formations of **5**, **4**, and **3** were explained by stepwise additions of **2** to zinc chloride based upon a view that these complexes are the adducts of **2** with zinc chloride in molar ratios of 1: 1, 2: 1, and 3: 1. Analogously, the correlation of the known polynuclear zinc complexes was systematically rationalized by stepwise additions of L_2Zn (L=ligand) to ZnX_2 (X=Cl or OH) or ZnO.

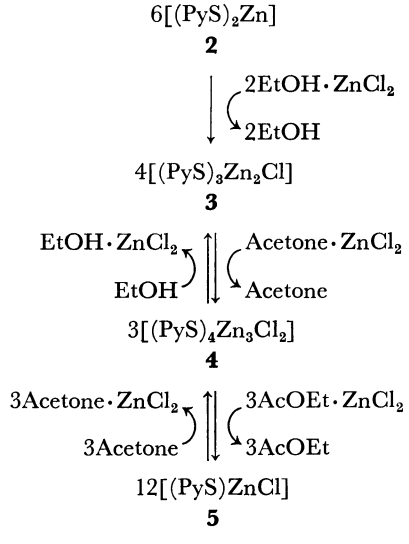
In a previous paper,[1] we reported on the formation of oxohexakis[2(1*H*)-pyridinethionato]tetrazinc (**1**) from bis[2(1*H*)-pyridinethionato]zinc (**2**)[2] and on the mutual transformations between **1** and **2**. Various types of polynuclear zinc complexes have been reported. They include L_8Zn_5O (L=ligand group),[2] L_6Zn_4O,[3] L_2Zn_2O,[4] L_5Zn_3X (X=chlorine atom or hydroxyl group),[5] $L_4Zn_4X_4$,[6] $L_4Zn_3X_2$,[7] and L_3Zn_2X[8] type complexes. The types of complexes are different depending on the kind of the ligand. Correlations between these types of complexes have not been elucidated, probably owing to the lack of report on the formation of different type of polynuclear zinc complexes formed with the same ligand.[9]

This paper describes the syntheses of chlorozinc complexes, L_3Zn_2Cl, $L_4Zn_3Cl_2$, and LZnCl where L is 2(1*H*)-pyridinethionato group, and mutual transformations among the three complexes and the complexes **1** and **2**, which contribute a systematization of polynuclear zinc complexes.

Results and Discussion

The transformation of **2** into oxocomplex **1** has been explained by the fission of one of four 2(1*H*)-pyridinethionato ligands in the complex **2**.[1,2] When **2** was treated with a half-molar equivalent of benzoyl chloride in 1,2-dichloroethane (EDC), one of four 2(1*H*)-pyridinethionato groups was removed as the *S*-benzoyl derivative, and chlorotris[2(1*H*)-pyridinethionato]dizinc (**3**) was obtained quantitatively. The complex **3** is a new complex and the characterization will be described later. The complex **3** was also obtained by a reaction of **2** with zinc chloride in a molar ratio of 3: 1 in diethyl ether. A treatment of **2** with a large excess molar amount of zinc chloride (in a molar ratio of 1: 1) in ethanol gave **3**, but the same reaction in acetone afforded another product, dichlorotetrakis[2(1*H*)-pyridinethionato]trizinc (**4**). The complex **4** could be obtained by the reaction of **3** with an excess molar amount of zinc chloride (in a molar ratio of 2: 3) in acetone. When **2** was treated with an excess molar amount of zinc chloride (in a molar ratio of 1: 2) in ethyl acetate, the third complex, chloro[2(1*H*)-pyridinethionato]zinc (**5**) was isolated. The complex **5** could be obtained also by the treatment of **4** with zinc chloride in ethyl acetate. The complexes **4** and **5** are also new compounds and the characterization will be described later. When **5** was treated in acetone, **4** was recovered. The treatment of **4** in ethanol gave **3**. The complexes **3**, **4**, and **5** all could be converted to oxocomplex **1** when they were treated in boiling water.

The experimental results for the formation of the complexes can be rationalized as shown in Scheme 1.



PyS=2(1*H*)-pyridinethionato

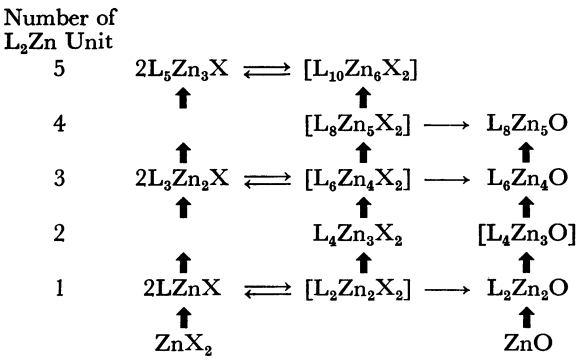
Scheme 1.

The formation of a product in a specific solvent can be rationalized by a ligand exchange reaction of zinc chloride between the reactant and the solvent.

The complexes **3**, **4**, and **5** can be viewed as adducts of bis[2(1*H*)-pyridinethionato]zinc with zinc chloride in molar ratios of 3: 1, 2: 1, and 1: 1, respectively. The complex **1** is on a same level with the complex **3**, since **1** is an adduct of bis[2(1*H*)-pyridinethionato]zinc with zinc oxide in a molar ratio of 3: 1.

In a similar idea various types of polynuclear zinc complexes reported hitherto can be made systematic as shown in Scheme 2, in which a thick arrow signifies an addition of a unit of L_2Zn. A stepwise addition of L_2Zn to ZnX_2 or ZnO leads to a formation of each level of zinc complexes. The several types of complexes put in brackets are not yet reported. The stability of

complex could be depend on the kind of the ligand and the conditions under which the formation was performed. The solvent is a very important factor as illustrated in Scheme 1 for 2(1*H*)-pyridinethionato zinc complexes. From Scheme 2, one can predict the presence of complexes containing four and five units of $(PyS)_2Zn$, $(PyS)_8Zn_5Cl_2$ or $(PyS)_8Zn_5O$ and $(PyS)_{10}Zn_6Cl_2$ or $(PyS)_5Zn_3Cl$, but they are not yet isolated. One may be able to isolate them when appropriate solvents are found.



Scheme 2. Complex types (complexes in brackets are unknown).

In a previous report,[1] we have described a probable formation of oxobis[2(1*H*)-pyridinethionato]dizinc in the reaction of 2(1*H*)-pyridinethione and zinc oxide in a molar ratio of 2: 1 in water. Oxotetrakis[2(1*H*)-pyridinethionato]trizinc can be estimated to be produced in an appropriate solvent, since the same level chlorocompound **4** is moderately stable.

Characterization of the Complexes. The compositions of the three complexes **3**, **4**, and **5** were determined by elemental analyses (C, H, Cl, N, and S). The complexes **3**, **4**, and **5** were obtained as powdery crystals, respectively. The powder X-ray analyses showed the independent spectrum for the three complexes and the contamination of free zinc chloride in the complexes was not observed.

Thermal analysis curves of **3**, **4**, and **5** show single and sharp endothermic peaks at 297, 303, and 295 °C, respectively. The mixture prepared by mixing any two of the complexes **2**, **3**, **4**, and **5** give thermal analysis curves showing broad endothermic peaks at temperatures different from those of the endothermic peaks for **2**, **3**, **4**, and **5**, except the mixture of **4** and **5** whose curve shows a sharp endothermic peak but at 287 °C. These facts indicate for the three complexes **3**, **4**, and **5** to be independent compounds, respectively.

The IR spectrum of the complex **3** exhibits bands due to C=C/C=N stretching vibration at 1595 (s), 1555 (s), 1445 (s), and 1420 cm^{-1} (s), a band due to C=S stretching vibration at 1135 cm^{-1} (s), bands due to ring vibration at 1020 (m) and 650 cm^{-1} (w), and bands due to C–H bending vibration at 770 (s), 765 (sh), and 760 cm^{-1} (sh). The absorption patterns of the corresponding bands in **1**, **2**, **4**, and **5** are similar to that of bands in **3**, except that the spectrum of **2** shows doublet peaks or peaks with a shoulder at 1455, 1420, 1020, and 645 cm^{-1} and that the spectrum of **4** and **5** show a doublet peak or a peak with a shoulder at 650 cm^{-1}. The fact thet the absorption patterns of these bands of **3**, **4**, and **5** are similar to that of the bands of **1** indicates that the 2(1*H*)-pyridinethionato ligands act as bidentates and bridging ligands in the complexes **3**, **4**, and **5**.[1]

The mass spectra of **3**, **4**, and **5** exhibit several fragmentation ions containing zinc, 2(1*H*)-pyridinethionato ligand, and/or chlorine. The peak pattern of the MS spectra of **3**, **4**, and **5** differ depending on the temperature of the inlet part to which the samples were introduced. The peak pattern of the MS feature higher than *m/e* 209[(PyS)ZnCl] are shown in Table 1. The changes of peak patterns of the three compounds depending on

Table 1. Mass spectral data for thionatozinc complexes (*m/e*)

Compound	Temperature[a] 120 °C	150 °C	180 °C
$(PyS)_3Zn_2Cl$ **3**	458[$(PyS)_3Zn_2$] 284[$(PyS)_2Zn$] 209[(PyS)ZnCl)]	458[$(PyS)_3Zn_2$] 284[$(PyS)_2Zn$] 209[(PyS)ZnCl]	490[$(PyS)_3Zn_2S$] 458[$(PyS)_3Zn_2$] 284[$(PyS)_2Zn$] 220[$(PyS)_2$] 209[(PyS)ZnCl]
$(PyS)_4Zn_3Cl_2$ **4**		458[$(PyS)_3Zn_2$] 284[$(PyS)_2Zn$] 209[(PyS)ZnCl]	490[$(PyS)_3Zn_2S$] 458[$(PyS)_3Zn_2$] 394[$(PyS)_3Zn$] 383[$(PyS)_2Zn_2Cl$] 362[$(PyS)_2$(py)Zn] 284[$(PyS)_2Zn$] 220[$(PyS)_2$] 209[(PyS)ZnCl]
$[(PyS)ZnCl]_n$ **5**	284[$(PyS)_2Zn$] 209[(PyS)ZnCl]	284[$(PyS)_2Zn$] 209[(PyS)ZnCl]	458[$(PyS)_3Zn_2$] 383[$(PyS)_2Zn_2Cl$] 362[$(PyS)_2$(py)Zn] 284[$(PyS)_2Zn$] 209[(PyS)ZnCl]

a) The temperature at which the spectra were measured.

the temperature are clearly different, respectively. This phenomena can not be rationalized at present, but the results indicate that the complexes **3**, **4**, and **5** are independent compounds. Although there is no certain evidence, **5** seems to be not monomeric. This is suggested by the high melting point of **5** and by MS peak of **5** at *m/e* 284[$(PyS)_2Zn$] which was observed in the spectra measured even at 120 °C.

Experimental

All melting points were determined in a liquid bath unless otherwise mentioned and were uncorrected. The powder X-ray diffraction was measured on a Rigaku D_2 X-ray diffractometer. The thermal analyses were performed on a Rigaku 8085 differencial scanning calolimeter. The IR spectra were measured in KBr disks with a Hitachi Perkin-Elmer 225 and a Hitachi EPI-G2 grating infrared spectrometer. The mass spectra were measured with a Hitachi M52 mass spectrometer.

Materials. Commercial anhydrous zinc chloride was used after drying over diphosphorus pentaoxide. Bis[2(1*H*)-pyridinethionato]zinc (**2**) was prepared by the method previously reported.[1] Commercial benzoyl chloride was distilled before its use.

Chlorotris[2(1H)-pyridinethionato]dizinc (3). a) Reaction of 2 with Zinc Chloride in Ethanol: A solution of zinc chloride (95 %, 0.43 g, 3.0 mmol) in ethanol (30 ml) was added to a suspension of **2** (0.86 g, 3.0 mmol) in ethanol (40 ml) with stirring at room temperature and the mixture was stirred at room temperature for 12 h. The precipitate was collected by filtration, washed with ethanol (80 ml), and dried at 70 °C for 24 h under reduced pressure to give 0.98 g (98%) of colorless crystalline powder; mp 294—298 °C. Found: C, 36.35; H, 2.57; Cl, 7.09; N, 8.16; S, 19.14%. Calcd for $C_{15}H_{12}ClN_3S_3Zn_2$: C, 36.27; H, 2.44; Cl, 7.14; N, 8.46; S, 19.37%. Molecular weight of the product could not be determined owing to the poor solubility in most organic solvent except *N,N*-dimethylformamide, in which the product was partly hydrolyzed with a slight amount of water contained in the solvent.

b) Reaction of 2 with Zinc Chloride in Diethyl Ether: Zinc chloride (95%, 0.72 g, 5.0 mmol) was treated with **2** (4.29 g, 15.0 mmol) in diethyl ether (100 ml) at room temperature for 17 h. The precipitate was collected by filtration and washed with diethyl ether (20 ml) to give 4.93 g (99%) of **3** as colorless crystalline powder; mp 294—298 °C. The IR spectrum of the powder was identical with that of the product obtained in a). Thermal analysis curve of the solid exhibits an endothermic peak at 297 °C.[11]

c) Reaction of 2 and Benzoyl Chloride: A solution of benzoyl chloride (2.81 g, 20 mmol) in 1,2-dichloroethane (EDC) (40 ml) was added drop by drop to a suspension of **2** (11.43 g. 40 mmol) in EDC (110 ml) with stirring at room temperature and the mixture was stirred for 18.5 h. The precipitate was collected by filtration and washed with EDC (20 ml) to give 9.90 g (100%) of **3** as colorless crystalline powder. The IR spectrum of the powder was identical with that of the product obtained in a). The filtrate separated from **3** and washings were combined and concentrated under reduced pressure. Diethyl ether (70 ml) was added to the residue and filtered leaving insoluble materials. A solution of zinc chloride (95%, 1.38 g, 9.6 mmol) in diethyl ether (50 ml) was added to the filtrate and the mixture was stirred at room temperature for 21.5 h. The precipitate was collected by filtration and washed with diethyl ether (20 ml) to give 4.74 g (84%) of bis(2-benzoylthiopyridine)dichlorozinc (**6**) as colorless solid. The IR spectrum of the solid was identical with that of authentic sample.

Bis(2-benzoylthiopyridine)dichlorozinc (6). A solution of zinc chloride (95%, 0.72 g, 5 mmol) in diethyl ether (30 ml) was added drop by drop to a solution of 2-benzoylthiopyridine[12] (2.15 g, 10 mmol) in diethyl ether (20 ml) with stirring at room temperature. The precipitate was collected by filtration and washed with diethyl ether (20 ml) to give 2.73 g (96 %) of colorless powder; mp 182—185 °C. Found: C, 50.76; H, 3.05; Cl, 12.67; N, 4.70; S, 11.19%. Calcd for $C_{24}H_{18}Cl_2N_2O_2S_2Zn$: C, 50.85; H, 3.20; Cl, 12.51; N, 4.94; S, 11.31%.

Dichlorotetrakis[2(1H)-pyridinethionato]trizinc (4). a) Reaction of 2 with Zinc Chloride: A solution of zinc chloride (95%, 4.30 g, 30 mmol) in acetone (45 ml) was added to a suspension of **2** (8.57 g, 30 mmol) in acetone (150 ml) with stirring at room temperature and then the mixture was stirred at room temperature for 4 h. The precipitate was collected by filtration and washed with acetone (90 ml) to give 10.48 g (99%) of colorless crystalline powder; mp 305—308 °C. Thermal analysis curve of the powder exhibits an endothermic peak at 303 °C. Found: C, 33.72; H, 2.28; Cl, 10.13; N, 7.75; S, 17.89%. Calcd for $C_{20}H_{16}Cl_2N_4S_4Zn_3$: C, 33.94; H, 2.28; Cl, 10.02; N, 7.94; S, 18.12%. Molecular weight of the product could not be determined owing to the poor solubility in most organic solvent except *N,N*-dimethylformamide, in which the product was partly hydrolyzed with a slight amount of water contained in the solvent.

b) Reaction of 3 with Zinc Chloride: Zinc chloride (95%, 0.27 g, 1.8 mmol) was treated with **3** (0.60 g, 1.2 mmol as monomer) in acetone (110 ml) at room temperature. The mixture was refluxed for 3 h and stirred at room temperature for 7 h. The precipitate was collected by filtration and washed with acetone (50 ml) to give 0.63 g (99%) of **4** as colorless solid; mp 304—307 °C. The IR spectrum of the solid was identical with the product obtained in *a)*.

Chloro[2(1H)-pyridinethionato]zinc (5). a) Reaction of 2 with Zinc Chloride: A solution of zinc chloride (95%, 0.44 g, 3.0 mmol) in ethyl acetate (50 ml) was added to a suspension of **2** (0.43 g, 1.5 mmol) in ethyl acetate (40 ml) with stirring at room temperature and then the mixture was refluxed for 5 h. The precipitate was collected by filtration and washed with ethyl acetate (100 ml) under dried nitrogen atmosphere to give 0.62 g (98%) of colorless crystalline powder; mp 296—298 °C. Thermal analysis curve of the powder exhibits an endothermic peak at 295 °C. Found: C, 28.65; H, 1.66; Cl, 16.95; N, 6.50; S, 15.31%. Calcd for $C_5H_4ClNSZn$: C, 28.46; H, 1.91; Cl, 16.80; N, 6.64; S, 15.20%.[13]

b) Reaction of 4 with Zinc Chloride: Zinc chloride (95%, 0.43 g, 3.0 mmol) was treated with **4** (1.06 g, 1.5 mmol as monomer) in ethyl acetate (80 ml) at room temperature. The mixture was refluxed for 4 h and stirred at room temperature for 9 h. The reaction mixture was treated in the similar manner as in a) to give 1.19 g (94%) of **5** as colorless crystalline powder; mp 296—298 °C. The IR spectrum of the powder was identical with the product obtained in *a)*.

Transformation of 5 into 4 in Acetone. A suspension of **5** (4.22 g, 20 mmol as monomer) in acetone (100 ml) was refluxed for 35 h. The precipitate was collected by filtration and washed with acetone to give 3.43 g (5 mmol, 97%) of **4** as colorless crystalline powder; mp 304—307 °C. The IR spectrum of the powder was identical with that of **4** obtained above. A solution of triphenylphosphine oxide (1.26 g, 4.5 mmol) in acetone (50 ml) was added to a portion (30.0 g) of the combined solution (85.9 g) of the filtrate separated from **4** and washings. The mixture was concentrated under reduced pressure and the residue was treated with ethyl acetate (50 ml). The insoluble materials were collected by filtration and washed with ethyl

acetate (30 ml) to give 1.08 g of colorless solid; mp 236—241 °C (on a hot plate). The IR spectrum of the solid was identical with that of authentic dichlorobis(triphenylphosphine oxide)-zinc.[14] This result shows that at least 4.5 mmol (89%) of zinc chloride is generated by the above treatment of **5** in acetone.

Transformation of 4 into 3 in Ethanol. A suspension of **4** (4.25 g, 6 mmol as monomer) in ethanol (100 ml) was refluxed for 9 h. The precipitate was collected by filtration and washed with ethanol (50 ml) to give 3.83 g (7.7 mmol, 96%) of **3** as colorless crystalline powder; mp 298—300 °C. The IR spectrum of the powder was identical with that of **3** obtained above. A solution of triphenylphosphine oxide (1.45 g, 5.2 mmol) in ethanol (20 ml) was added to the combined solution of the above filtrate and washings. The mixture was concentrated under reduced pressure and the residue was treated with ethyl acetate (50 ml). The insoluble materials were collected by filtration and washed with ethyl acetate to give 1.36 g of colorless solid; mp 236—240 °C (on a hot plate). The IR spectrum of the solid was identical with that of authentic dichlorobis-(triphenylphosphine oxide)zinc.[14] This result shows that 2.0 mmol (100%) of zinc chloride is generated by the above treatment of **4** in ethanol.

Hydrolysis of 3 in Water. A suspension of **3** (1.49 g, 3 mmol as monomer) in water (100 ml) was refluxed for 1 h. The precipitate was collected by filtration and washed with water (40 ml) to give 1.06 g (1.1 mmol) of **1** as colorless crystalline powder; mp above 340 °C (gradually dec).[15] The IR spectrum of the powder was identical with that of authentic sample **1**. The filtrate separated from **1** and washings were combined and the mixture was concentrated under reduced pressure. Ethyl acetate (50 ml) was added to the residue and the mixture was stirred. The insoluble materials were collected by filtration and washed with ethyl acetate (15 ml) to give 0.38 g (1.1 mmol, of dichlorobis[2(1*H*)-pyridinethione]zinc (**7**) as slightly yellowish crystalline powder; mp 248—256 °C (on a hot plate). The IR spectrum of the powder was identical with that of authentic sample **7**.[16] The filtrate separated from **7** and washings were combined and mixed with a solution of triphenylphosphine oxide (0.31 g, 1.1 mmol) in ethyl acetate (30 ml). The precipitate was collected by filtration and washed with ethyl acetate to give 0.27 g (0.4 mmol) of dichlorobis(triphenylphosphine oxide)zinc as slightly yellowish solid; mp 235—239 °C (on a hot plate). The IR spectrum of the solid was identical with that of authentic sample.[14]

Hydrolysis of 4 in Water. A suspension of **4** (4.25 g, 6 mmol as monomer) in water (100 ml) was refluxed for 2 h. The reaction mixture was treated in a similar manner as in the hydrolysis of **3**. The products were 2.76 g (2.9 mmol) of **1**; mp above 340 °C (gradually dec),[15] 1.00 g (2.8 mmol) of **7**; mp 246—254 °C (on a hot plate), and 2.11 g (3.0 mmol) of dichlorobis(triphenylphosphine oxide)zinc; mp 236—239 °C (on a hot plate). The IR spectra of the products were identical with those of authentic samples.

Hydrolysis of 5 in Water. A suspension of **5** (1.69 g, 8 mmol as monomer) in water (70 ml) was refluxed for 1 h. The reaction mixture was treated in a similar manner as in the hydrolysis of **3**. The products were 0.93 g (1.0 mmol) of **1**; mp above 340 °C (gradually dec),[15] 0.32 g (0.9 mmol) of **7**; mp 245—255 °C (on a hot plate), and 2.04 g (2.9 mmol) of dichlorobis(triphenylphosphine oxide)zinc; mp 238—242 °C (on a hot plate). The IR spectra of the products were identical with those of authentic samples.

References

1) M. Masaki, S, Matsunami, T. Kimura, and T. Oshima, *Bull. Chem. Soc. Jpn.*, **52**, 502 (1979).

2) Bis[2(1*H*)-pyridinethionato]zinc has been estimated to be dimeric based on the data of mass spectrum and osmometric molecular weight determination.[1] However, since the result is not conclusive, molar ratios of **2** and other reagents in the reactions were calculated based on $(C_5H_4NS)_2Zn$ unit in this report.

3) M. Braid and R. H. Schmitt, Fr. Patent 1525721 (1968); *Chem. Abstr.*, **71**, 14839h (1969).

4) H. Koyama and Y. Saito, *Bull. Chem. Soc. Jpn.*, **27**, 112 (1954); J. Charalambous, R. G. Copperthwaite, S. W. Jeffs, and D. E. Shaw, *Inorg. Chim. Acta*, **14**, 53 (1975); A. J. Burn and G. W. Smith, *Chem. Commun.*, **1965**, 394; S. Meriani, G. Nardin, and A. Ripamonti, *Inorg. Chem.*, **6**, 1931 (1967); M. Corbett and B. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, **6**, 261 (1970); D. Johnstone, J. E. Fergusson, and W. T. Robinson, *Bull. Chem. Soc. Jpn.*, **45**, 3721 (1972).

5) T. Mito, S. Nara, M. Nagata, and M. Yukitomi, Japan Patent, 21419 (1974); *Chem. Abstr.*, **82**, 99229j (1976).

6) J. P. Farve, *Bull. Soc. Chim. Fr.*, **1968**. 237.

7) L. J. Porter, D. D. Perrin, and R. W. Hay, *J. Chem. Soc., A*, **1969**, 118.

8) J. D. Citron and R. E. Tarney, Ger. Offen. Patent 2513778 (1975); *Chem. Abstr.*, **84**, 32375b (1976).

9) a) S. Komura, R. Harima, T. Misawa, T. Goto, T. Masatomi, T. Nishi, Y. Shimizu, and Y. Nakacho, Japan Kokai Patent 70343 (1975); *Chem. Abstr.*, **83**, 178576u (1975); M. Z. Gurevich, T. M. Sas, V. V. Zelentsov, B. D. Stepin, and N. E. Mazzpova, *Zh. Neorg. Khim.*, **20**, 452 (1975); *Chem. Abstr.*, **82**, 179843v (1975); V. V. Sher, E. I. Markova, L. G. Khanakova, G. N. Kuz'mina, and P. I. Sanin, *Neftekhimiya*, **13**, 876 (1973); *Chem. Abstr.*, **89**, 95168z (1974); b) S. Kacani and L. Stefanka, Czech. Patent 124384 (1967).

10) Two types of complexes formed with 2(3*H*)-benzothiazolethionato ligand have been reported independently.[6,9b] But it is not clear whether the products described in the papers are identical or not, since no characterization of the products have been demonstrated, unfortunately.

11) For the preparation of **3**, diethyl ether is recommended for the reaction solvent, since the perfect removal of the solvent from the product is easy.

12) Y. Ueno, S. Asakawa, and E. Imoto, *Nippon Kagaku Zasshi*, **89**, 101 (1968).

13) When the same reaction was carried out by stirring the mixture of **2** and zinc chloride in ethyl acetate at room temperature for 2 h and the precipitate was collected by filtration under undried atmosphere, the product obtained was different from **5**. Mp 293—298 °C. The IR spectrum of the product exhibits medium intensity bands at 1590, 1510, and 1370 cm^{-1} in addition to bands of **5** and shows a medium intensity multiplet around 3100 cm^{-1}, while the intensity of the corresponding band in **5** is weak.

14) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **80**, 262 (1906).

15) In the measurement of mp, it was observed that the product began to be colored gradually at about 340 °C and melted at 380—385 °C with decomposition.

16) For the preparation of **7**, an aqueous solution of zinc chloride was used instead of its ethanolic solution in the previous paper: B. P. Kennedy and A. B. P. Lever, *Can. J. Chem.*, **50**, 3488 (1972).