a calculation using 75 k points in half of the zone. The other half of the zone simply yields complex conjugate wave functions that need not be calculated, but for the purposes of estimating r_0 in the above formula, $N_k = 150$. The same set of k points was used for the $H_{0.33}MS_2$ computations. For ZrS, computations for the construction of Wannier functions were carried out by using 225 k points ($N_k = 450$) spread over half of the three-dimensional Brillouin zone.

Supplementary Material Available: Extended Hückel band structure diagrams (dispersion curves) for ZrS, Mo_3S_6 (MoS_2 calculated with a $3^{1/2} \times 3^{1/2}$ supercell), MoS_2, and HMo_3S_6 ($=H_{0.33}MoS_2$). (4 pages). Ordering information is given on any current masthead page.

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Preparation of ZnS and CdS by Thermal Degradation of (Methanethiolato)zinc and -cadmium Complexes, $[M(SMe)_2]_n$ (M = Zn, Cd)

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Reactions of aqueous MeSNa with $ZnCl_2$ and with $CdCl_2$ give the methanethiolato complexes $[Zn(SMe)_2]_n$ (**1a**) and $[Cd(SMe)_2]_n$ (**2**), respectively. Reaction of MeSH with $ZnEt_2$ in hexane also gives $[Zn(SMe)_2]_n$ (**1b**). $[Zn(SEt)_2]_n$ (**3**) and $[Zn(S\text{-}i\text{-}Pr)_2]_n$ (**4**) are obtained by reaction of EtSLi and *i*-PrSLi with ZnI_2, respectively. Elemental analyses of the complexes give satisfactory results. Peaks in the X-ray diffraction pattern of **1b** are considerably broader than those of **1a**. Thermolysis of **1a** and **1b** at 260 °C gives β-ZnS accompanied by evolution of MeSMe in almost quantitative yields. Thermolysis of **2** under similar conditions give CdS as a mixture of α- and β-forms. Thermogravimetric analyses of the thiolato compounds also suggest elimination of MeSMe in the vicinity of 230–240 °C. TG curves of **1b** and **2** at constant temperatures indicate that the thermolysis obeys first-order kinetics in $[M(SMe)_2]_n$. Activation parameters of the reactions are 143 and 191 kJ mol^{-1}, respectively. Thermolysis of **1a** obeys autocatalytic type kinetics expressed by the kinetic equation $\ln [x/(1 - x)] = kt + C$ (x: reacted fraction). Heating the (ethanethiolato)zinc complex **3** gives ZnS similarly to the case of **1a**, **1b**, and **2**, while thermolysis of **4** is much slower than the reactions of these complexes.

Introduction

Sulfides of several transition metals show interesting electrical and optical properties such as semiconductivity, luminescence, and photoconductivity.[1] Degradation of metal complexes with sulfur-containing ligands seems to be an attractive method for the preparation of metal sulfides because some of these complexes have sufficiently high vapor pressure or low decomposition temperature to be used as the materials for the CVD (chemical vapor deposition) process. Various transition-metal alkoxides have already been used as materials for metal oxide deposition by the MOCVD method and the sol–gel technique.[2] These procedures involve C–O bond cleavage of the alkoxide group ligating to the metal center under the reaction conditions. Since C–S bond dissociation energy is smaller than that of the corresponding C–O bond,[3] transition-metal thiolato complexes are promising as materials for metal sulfide preparation through C–S bond cleavage of the thiolato ligands.

Previously C–S bond cleavage reactions of several transition-metal thiolato complexes were reported to proceed under mild conditions.[4–9] We have also reported that bis(benzenethiolato)nickel(II) complexes having bipyridine or tertiary phosphines as auxiliary ligands gave PhSPh both in the solid state and in solution.[10]

$$\mathrm{Ni(SPh)_2L_2} \xrightarrow{\Delta} \mathrm{PhSPh} \qquad (1)$$

$$\mathrm{L = PEt_3,\ {}^1\!/_2\ bpy}$$

Although the metal-containing products found in (1) were mixtures of several uncharacterized compounds due to coordination of the auxiliary organic ligands to the products, yields of PhSPh were almost quantitative in the reactions. These observations suggested that degradation of homoleptic thiolato compounds of bivalent transition metals, $M(SR)_2$, would give the metal sulfides accompanied by evolution of RSR according to the equation

$$\mathrm{M(SR)_2 \rightarrow MS + RSR} \qquad (2)$$

An ionic (thiolato)zinc complex has been reported to catalyze photodecomposition of water by using THF sacrificial reagent.[11] In the reaction ZnS, formed by partial decomposition of the complex under the reaction conditions, was responsible for the photodecomposition of water.[12]

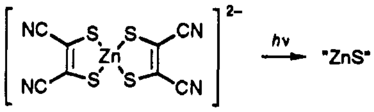

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Table I. Analytical and IR Data for **1a**–**4**

complex	anal.[a]/% C	H	Zn or Cd	IR:[b] wavenumber/cm^{-1}
$[Zn(SMe)_2]_n$ (**1a**)	14.8 (15.1)	3.9 (3.8)	40.5 (41.0)	2980 (w), 2930 (w), 2850 (w), 1433 (s), 1321 (s), 962 (vs), 696 (s), 422 (m), 411 (m)
$[Zn(SMe)_2]_n$ (**1b**)	15.0 (15.1)	3.8 (3.8)	40.6 (41.0)	*c*
$[Cd(SMe)_2]_n$ (**2**)	11.5 (11.6)	2.9 (2.9)	54.5 (54.4)	2980 (w), 2930 (w), 2840 (w), 1430 (s), 1328 (s), 970 (s), 688 (s)
$[Zn(SEt)_2]_n$ (**3**)	25.4 (25.6)	5.5 (5.3)	34.5 (34.9)	2980 (w), 2970 (m), 2930 (m), 2870 (w), 1448 (m), 1378 (m), 1264 (s), 975 (m), 767 (m), 658 (m), 510 (m)
$[Zn(S\text{-}i\text{-}Pr)_2]_n$ (**4**)	33.2 (33.4)	6.4 (6.5)	29.8 (30.3)	2970 (m), 2960 (s), 2920 (s), 2860 (m), 1452 (s), 1382 (m), 1362 (m), 1254 (s), 1158 (s), 1058 (s), 950 (w), 929 (w), 891 (w), 622 (s), 418 (w)

[a] Calculated values are in parentheses. [b] Abbreviation: vs, very strong; s, strong; m, medium; w, weak. [c] IR spectrum of **1b** is identical with that of **1a**.

Table II. Kinetic Results of the Thermal Decomposition of **1a**, **1b**, and **2**

complex	k/s^{-1} [a]
1a	3.64×10^{-3} (492), 6.89×10^{-3} (501), 8.07×10^{-3} (507)
1b	1.15×10^{-3} (483), 1.76×10^{-3} (490), 2.21×10^{-3} (493), 3.39×10^{-3} (498), 3.91×10^{-3} (501), 5.75×10^{-3} (505)
2	2.25×10^{-3} (488), 3.28×10^{-3} (493), 4.75×10^{-3} (497), 8.57×10^{-3} (503), 1.42×10^{-2} (508)

[a] For the thermolysis of **1a**, the rate constant is based on the kinetic equation $\ln [x/(1-x)] = kt + C$ (x: reacted fraction). For **1b** and **2** the rate constant is based on simple first-order kinetics. See text. Temperature (K) is shown in parentheses.

The presence of ZnS in the reaction mixture was confirmed by means of X-ray diffraction. However, reaction 3 is not suitable for preparation of ZnS due to the low conversion of the complex into ZnS under the reaction conditions. All these results prompted us to investigate degradation of "$Zn(SR)_2$" and "$Cd(SR)_2$" to prepare ZnS and CdS, which are utilized as materials for electrical and optical devices as well as photocatalysts.

We have preliminarily reported formation of ZnS and CdS by thermolysis of the methanethiolato complexes of zinc and cadmium, $[Zn(SMe)_2]_n$ and $[Cd(SMe)_2]_n$, respectively.[13] Lead complexes with arenethiolato ligands, $Pb(SPh)_2$, $Pb(SC_6H_4Me)_2$, and $Pb(SC_6H_4Cl)_2$, have been reported to give PbS by the reaction with sulfur at room temperature.[14] Very recently, several research groups also reported the preparation of thin films of transition-metal chalcogenides such as TiS, CdSe, and $CuInS_2$ by thermolysis of transition-metal complexes, $Ti(S\text{-}t\text{-}Bu)_4$, $[Cd(SePh)_2][Et_2PCH_2CH_2PEt_2]$, and $(i\text{-}Bu)_2In(S\text{-}n\text{-}Pr)Cu(S_2CNBu_2)_2$, respectively.[15-17] Here we report full details of the preparation, characterization, and thermolysis behavior of the zinc and cadmium methanethiolato compounds as well as the preparation of the related alkanethiolato complexes of zinc.

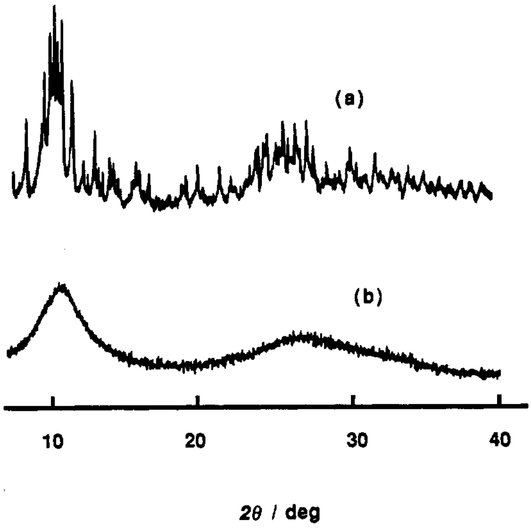

Figure 1. X-ray diffraction patterns of (a) **1a** and (b) **1b**. Measurement conditions: graphite-monochromated Cu Kα radiation; room temperature; scan rate 0.04° min^{-1}.

Results

The preparations of the thiolato complexes of zinc and cadmium in this work are summarized in eqs 4–6. Results of analysis and

$$MCl_2 + 2MeSNa \rightarrow (1/n)[M(SMe)_2]_n \tag{4}$$

1a: M = Zn
2: M = Cd

$$ZnEt_2 + 2MeSH \rightarrow (1/n)[Zn(SMe)_2]_n \tag{5}$$

1b

$$ZnI_2 + 2RSLi \rightarrow (1/n)[Zn(SR)_2]_n \tag{6}$$

3: R = Et
4: R = *i*-Pr

IR measurements are summarized in Table I. The methanethiolato compounds **1a**, **1b**, and **2** thermally decompose to give the corresponding metal sulfide. The reaction is summarized in eq 7. Kinetic reactions of the reactions obtained by thermo-

$$(1/n)[M(SMe)_2]_n \rightarrow MeSMe + MS \tag{7}$$

1a: M = Zn
1b: M = Zn
2: M = Cd

gravimetric measurements are summarized in Table II. These will be introduced at appropriate places in the sections that follow.

Discussion

Preparation and Characterization of Thiolato Complexes of Zinc and Cadmium. Reaction of MeSNa with 0.5 equiv of $ZnCl_2$ in aqueous solution gives $[Zn(SMe)_2]_n$ (**1a**) as a white solid. A similar reaction of MeSNa with $CdCl_2$ also gives $[Cd(SMe)_2]_n$ (**2**) in high yield. $[Zn(SMe)_2]_n$ (**1b**) is obtained also by reaction of MeSH with $ZnEt_2$ in hexane. The ethanethiolato complex $[Zn(SEt)_2]_n$ (**3**) and the 2-propanethiolato complex $[Zn(S\text{-}i\text{-}Pr)_2]_n$ (**4**) are prepared by reaction of RSLi (R = Et, *i*-Pr) with ZnI_2. The thiolato compounds show analytical data that agree well with the proposed formulas. Similar (arenethiolato)zinc complexes $[Zn(SAr)_2]_n$ have been already prepared by reaction of ZnO with ArSH or reaction of zinc salts with ArSNa and utilized as plasticizers.[18] Dance and co-workers prepared zinc and cadmium

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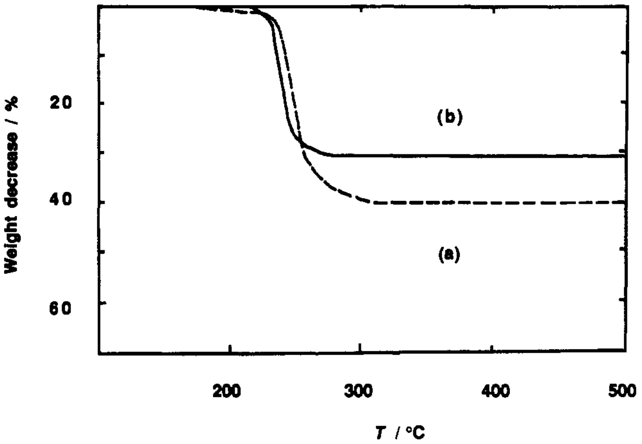

Figure 2. Thermogravimetric curves of (a) **1a** and (b) **2**. Measurements were performed under a stream of nitrogen. Rate of raising the temperature was 10 °C min^{-1} during the measurements.

arenethiolato compounds such as $Zn_4(SPh)_8(MeOH)$, $Cd(SPh)_2$, $Cd(SC_6H_4\text{-}p\text{-}Me)_2$, and $Cd_8(SC_6H_4\text{-}p\text{-}Br)_{16}(DMF)_3$ (DMF = *N*,*N*-dimethylformamide) and revealed their detailed structures by means of single-crystal X-ray diffraction.[19] These arenethiolato complexes have nonmolecular structures with adamantanoid cage units that are bonded to each other through the bridging thiolato ligands. Other thiolato cadmium complexes, $Cd(SCH_2COOEt)_2$[20] and $Cd(SCH_2CH_2OH)_2$,[21] were reported to have one- and two-dimensional nonmolecular structures, respectively. The alkanethiolato complexes **1a**–**4** are considered to have polymeric or nonmolecular structures with the bridging thiolato ligands functioning similarly to those in the above zinc and cadmium thiolato complexes; however, difficulty in crystal growth of **1a**–**4** prevented us from unambiguously determining the structures by single-crystal X-ray diffraction. Complexes **1a**, **1b**, and **2** were practically insoluble in many organic solvents such as Et_2O, $CHCl_3$, hexane, EtOH, and benzene and slightly soluble in acetone and DMF. The poor solubility is probably due to the polymeric structures.

Figure 1 shows X-ray diffraction patterns for complexes **1a** and **1b**. Complex **1a** shows many strong peaks at $2\theta = 9.5$–12.5 and 25–28°, while **1b** shows quite broad peaks centered at $2\theta = 11$ and 27°. This fact suggests that **1a** and **1b** have similar crystal structures and that **1b** has a much smaller particle size than **1a**.[22]

Thermolysis of 1a, 1b, and 2 To Give ZnS and CdS. Heating complexes **1a**, **1b**, and **2** at 260 °C under an argon atmosphere or in vacuo gave white (**1a**, **1b**) and orange (**2**) solids, respectively. Evolution of MeSMe in almost quantitative yields is observed by gas chromatographic analysis of the volatile products. Results of elemental analysis (metal and S) of the solid products agree with the calculated values for the metal sulfides although the products contain small amounts of carbon (0.6–0.8 wt %) and hydrogen (0.2–0.5 wt %). Further heating of the solid obtained from thermolysis of **1a** under an argon stream at 400 °C gives carbon-free product.

Thermogravimetric analysis of **1a**, **1b**, and **2** shows a sharp decrease in weight in the vicinity of 230–240 °C. Figure 2 shows the TG curves of **1a** and **2**. The weight decrease of the thiolato complexes during the measurement agrees with elimination of MeSMe from the complexes. DSC results for **2** indicate the occurrence of an exothermic reaction in the range 225–265 °C. The heat evolved during the reaction is determined to be 73 kJ mol^{-1}.

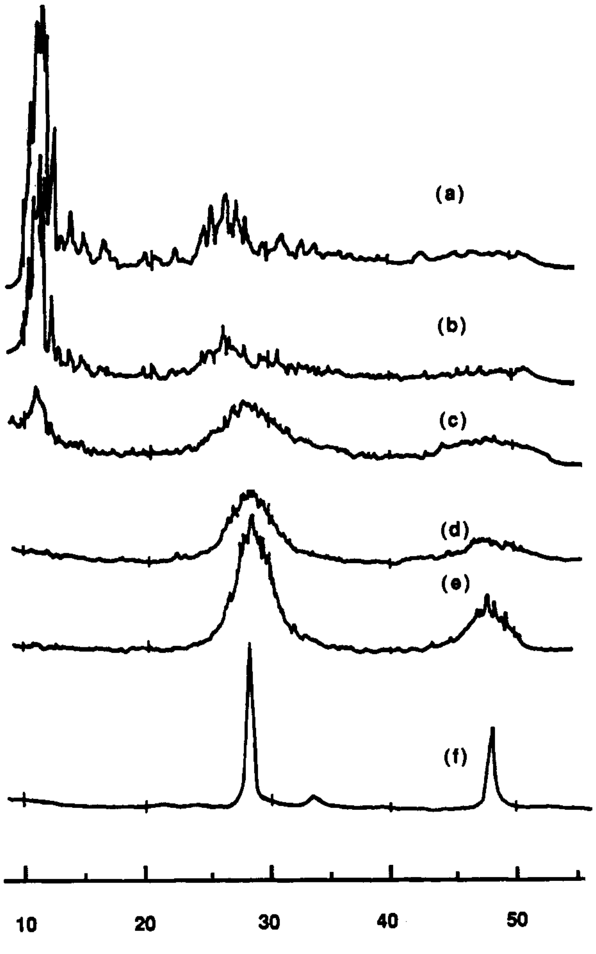

Figure 3. Change in X-ray diffraction patterns during thermolysis of **1a** at 260 °C; scan rate 2° min^{-1}. Conversion: (a) 0%; (b) 24%; (c) 67%; (d) 96%; (e) 100%; (f) after further heating at 400 °C for 3 h. Conversion of the reaction was monitored by measurement of the weight of the sample.

Figure 3 shows the change in X-ray diffraction patterns of **1a** during thermolysis.[23] Broadened peaks at about 29 and 48°, which are assigned to the diffraction of β-ZnS, grow with the decrease of the peaks due to **1a**. The diffraction patterns show neither broadening of the peaks due to **1a** nor the appearance of peaks due to compounds other than ZnS and **1a** throughout the reaction. The absence of a peak at $2\theta = 51.8°$, which corresponds to the (103) diffraction of α-ZnS, in the diffraction pattern of the product indicates exclusive formation of β-ZnS. Narrowing of the peaks due to (111) and (220) diffraction ($2\theta = 28.6$ and 47.6°, respectively) is observed at the late period of the reaction. After further heating at 400 °C for 3 h, the product shows sharp peaks at these positions.

Figure 4 shows the change in X-ray diffraction patterns during thermolysis of **2**. Broadened peaks due to CdS are observed in the reaction mixtures. The diffraction pattern of the final product shows a broadened small peak at $2\theta = 47.9°$, assignable to (103) diffraction of α-CdS, indicating the presence of a small amount

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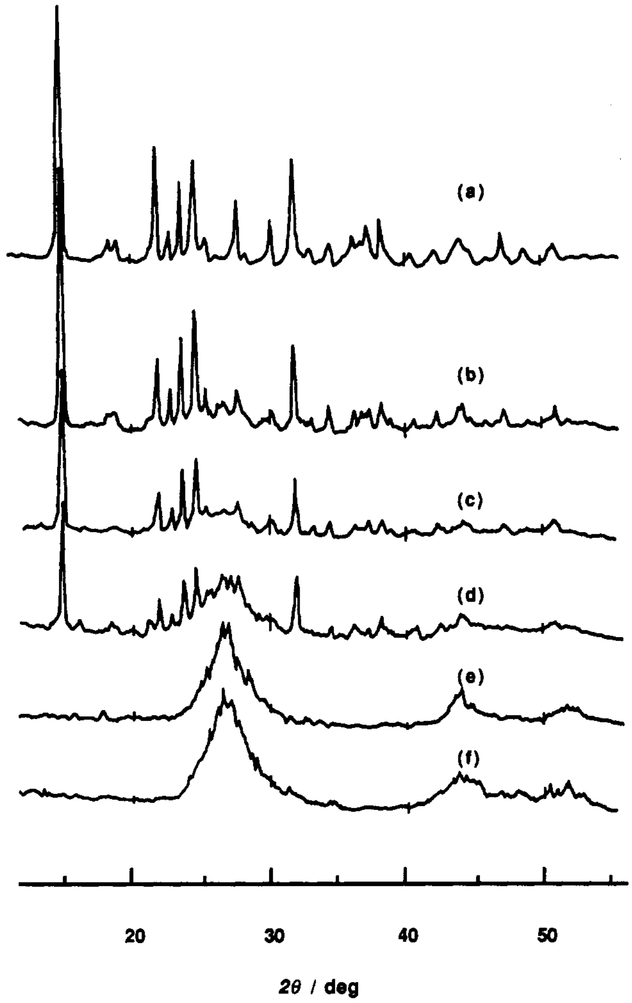

Figure 4. Change in X-ray diffraction patterns during thermolysis of **2** at 260 °C. Conversion: (a) 0%; (b) 11%; (c) 36%; (d) 59%; (e) 93%; (f) 100%.

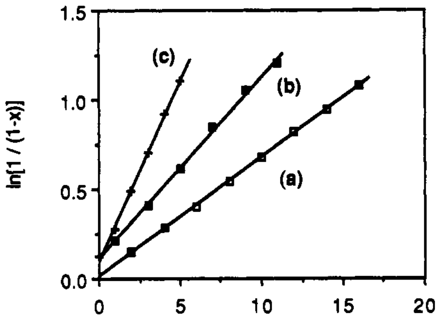

Figure 5. First-order plots of the thermolysis of **1b**. Temperature: (a) 210 °C; (b) 217 °C; (c) 225 °C.

of the α-form in the product. Further heating of the sample at 400 °C does not cause a change in the width of the peak near $2\theta = 26°$, which includes (100), (002), and (101) diffraction of the α-form and (111) diffraction of the β-form. Diffraction patterns of the product after further heating of the sample under argon atmosphere at 400 °C show sharp peaks due to α and β-CdS separately. However, a relative increase in the peak intensity of the α-form is also observed probably due to the transformation of the β- to the α-form under the conditions.[24]

All these results suggest that thermolysis of **1a**, **1b**, and **2** proceeds smoothly to give the corresponding metal sulfides accompanied by formation of MeSMe.

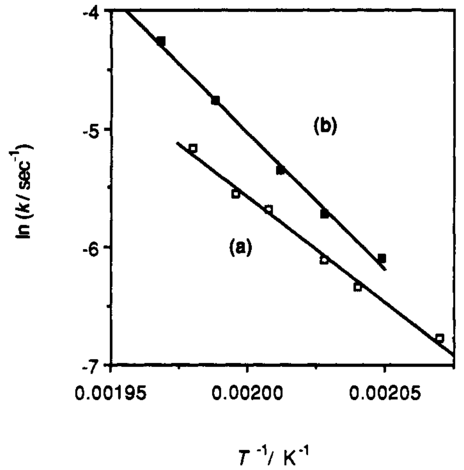

Figure 6. Arrhenius plots of the thermolyses of (a) **1b** and (b) **2**.

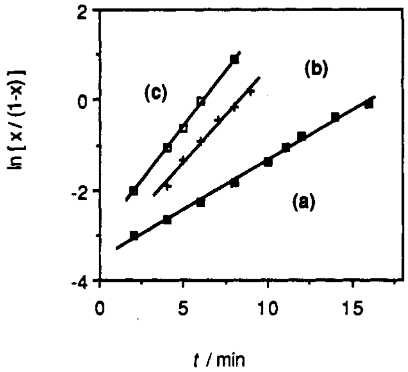

Figure 7. Plots of the thermolysis of **1a** based on the autocatalytic kinetic equation $\ln [x/(1-x)] = kt + C$ (x = reacted fraction). Temperature: (a) 219 °C; (b) 228 °C; (c) 234 °C.

Kinetics. The conversion of reaction 7 with time is followed by measurement of TG curves at constant temperatures. Figure 5 shows first-order plots of the thermolysis of **1b**. At these temperatures the reaction obeys first-order kinetics in the complex up to ca. 70% conversion. Thermolysis of **2** also obeys first-order kinetics. Activation energies obtained from the Arrhenius plots of the reactions (Figure 6) are 143 and 191 kJ mol^{-1}, respectively.

On the other hand, thermolysis of **1a** at similar temperatures does not obey simple first-order kinetics. The reaction rate is expressed by the equation

$$\ln [x/(1-x)] = kt + C$$

where x is the reacted fraction. This autocatalytic type of kinetics[25] is often applied to the analysis of solid-state reactions in which the rate-determining step is the diffusion of the gaseous product within the solid particles.[26] In the present study, thermolysis of complex **1a** obeys the above autocatalytic type of kinetics, while that of **1b** obeys first-order kinetics. This dichotomy can be attributed to the difference in the surface areas of the particles of these two complexes. Since particles of **1b** are considerably small as revealed by the large peak width of the X-ray diffraction pattern, diffusion of MeSMe within the particle is not involved in the rate-determining step.

The much smaller bulk density of **1b** compared to **1a** was noted as follows. One can place 18–20 mg of **1a** in an aluminum cell with a short cylinder shape (ca. 0.02-mL volume) for the thermogravimetry measurements, while more than 8 mg of **1b** cannot be placed in the same cell. This observation also seems to agree with the smaller particle size and consequential larger surface area of **1b** compared to **1a**.

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Thermolysis of $[Zn(SEt)_2]_n$ (3) and $[Zn(S\text{-}i\text{-}Pr)_2]_n$ (4). Thermolysis of complex **3** gives ZnS similarly to the reactions of **1a** and **1b**. However, thermolysis of **4** is slower than thermolysis of **1a**–**3**. Reaction of **4** at 260 °C for 8 h gives a mixture of propene, 2-propanethiol, and isopropyl sulfide. The propyl moiety contained in the organic products is ca. 34% of that expected from quantitative formation of ZnS from complex **4**. The obtained solid product contains 29 wt % carbon. These results suggest that thermolysis of **4** proceeds slowly under the reaction conditions and is not completed even after prolonged reaction.

Conclusion

Methanethiolato complexes of zinc and cadmium, $[Zn(SMe)_2]_n$ and $[Cd(SMe)_2]_n$, react thermally in the solid state to give the corresponding metal sulfides accompanied by evolution of MeSMe. β-ZnS is obtained cleanly by thermolysis of $[Zn(SMe)_2]_n$, while reaction of $[Cd(SMe)_2]_n$ gives CdS as a mixture of α- and β-forms. Thermolysis of $[Zn(SMe)_2]_n$ obeys first-order kinetics in the complex or autocatalytic type kinetics depending on the particle size. Analogous thermal reactions of zinc and cadmium thiolato complexes with higher solubility in organic solvents and higher vapor pressure may give ZnS and CdS as thin films. These thermolyses of transition-metal thiolato complexes will be applied to the preparation of various metal sulfides and related metal chalcogenides.

Experimental Section

MeSH and MeSNa (15% aqueous solution) were purchased from Tokyo Kasei Co. EtSLi was prepared by addition of EtSH to a hexane solution of BuLi (ca. 1.0 M) at 0 °C.

Elemental analyses (C, H, and S) were carried out by Dr. Masako Tanaka and Mr. Toyoharu Saito of our laboratory using a Yanagimoto CHN autocorder and a Yazawa halogen analyzer. Analyses of zinc and cadmium were performed by EDTA titration. IR spectra were recorded on a JASCO IR 810 spectrophotometer. X-ray diffraction patterns were obtained on a Phillips PW-1051 X-ray diffractometer using graphite-monochromated Cu Kα radiation. GC analyses were performed on a Shimadzu 3BT gas chromatograph using 5% SDC-550 or Porapak Q. DSC and TG measurements were carried out on a Shimadzu DT-30 thermal analyzer.

Preparation of $[Zn(SMe)_2]_n$ (1a) and $[Cd(SMe)_2]_n$ (2) by Reaction of MCl_2 (M = Zn, Cd) with MeSNa. $ZnCl_2$ (3.7 g, 27 mmol) was dissolved in water (100 mL). A small amount of undissolved solid was removed by filtration. Aqueous MeSNa (15%) (27 mL, ca. 4.1 g MeSNa) was added dropwise to the solution at room temperature to cause immediate precipitation of a white solid. The solid was separated from the solution by centrifugation followed by careful decantation of the solution from the mixture. Addition of water (100 mL) to the solid with stirring followed by the centrifugation and decantation procedure was repeated until no Cl^- was detected in the washings ($AgNO_3$). Drying the resulting white solid under vacuum gave $[Zn(SMe)_2]_n$ (**1a**) as a white powder (2.8 g, 65% based on Zn).

Preparation of $[Cd(SMe)_2]_n$ (**2**) was carried out analogously. Compound **2** was separated from the solution or the washings without centrifugation (yield 87%).

Preparation of $[Zn(SMe)_2]_n$ (1b) by Reaction of $ZnEt_2$ with MeSH. A hexane solution (10% v/v) of $ZnEt_2$ (2.4 g, 19 mmol) in a Schlenk flask equipped with a dry ice condenser and a dropping funnel was cooled at −30 °C under argon. MeSH (2.2 g, 46 mmol) was added dropwise from the dropping funnel. A white solid was precipitated immediately. The temperature of the mixture was raised gradually to room temperature. After the reaction mixture was maintained for several hours at that temperature, the white solid was filtered out with a glass tube equipped with a glass frit and washed with hexane several times.[27] Drying the solid under vacuum gave $[Zn(SMe)_2]_n$ (**1b**) (2.3 g, 72% based on Zn).

Preparation of $[Zn(SEt)_2]_n$ (3) and $[Zn(S\text{-}i\text{-}Pr)_2]_n$ (4). To an EtOH (20 mL) solution of ZnI_2 (1.05 g, 3.3 mmol) in a Schlenk flask was added EtSLi (0.45 g, 6.6 mmol) in EtOH (10 mL) slowly under a nitrogen atmosphere. The resulting solution became milky on stirring. Allowing the reaction mixture to settle overnight resulted in the separation of **3** as a white solid, which was filtered out, washed with H_2O until I^- was not detected in the washings ($AgNO_3$), and dried in vacuo (0.30 g, 49% yield based on Zn).

$[Zn(S\text{-}i\text{-}Pr)_2]_n$ (**4**) was prepared analogously (83% yield).

Thermolysis of 1a, 1b, and 2. A 200-mL flask containing **1b** (1.24 g, 7.8 mmol) was connected to a vacuum line through a glass tube having a side arm connected to a 50-mL flask. After evacuation of the system, **1b** was heated at 260 °C. The smaller flask was immersed in liquid N_2 to condense the volatile products. After reaction for 2 h, GC analysis of the organic product condensed in the flask revealed the formation of MeSMe (0.46 g, 95%). The remaining white solid gave analytical data that agreed with those of ZnS (0.76 g, 100%), although it contained small amounts of carbon and hydrogen. Anal. Calcd for ZnS: Zn, 67.1; S, 32.9; C, 0.0; H, 0.0. Found: Zn, 67.3; S, 31.2; C, 0.7; H, 0.4.

Further heating of the solid product was carried out in an electric furnace at 400 °C under a stream of argon. This procedure gave ZnS free of carbon. Anal. Found: Zn, 66.2; C, 0.0; H, 0.4.

Thermolysis of **1a** gave similar results.

Thermolysis of **2** (0.92 g) was carried out analogously. The color of the compound changed from white to orange during the reaction. Formation of MeSMe (99%) and CdS (97%) was observed. Anal. Calcd for CdS: Cd, 77.8; S, 22.2; C, 0.0; H, 0.0. Found: Cd, 76.8; S, 21.8; C, 0.6; H, 0.2.

Thermolysis of 3 and 4. Complex **3** (14 mg, 0.074 mmol) in the thermogravimetric apparatus was heated under a nitrogen stream up to 300 °C to cause decrease in the sample weight. The weight loss during the analysis agrees with the separation of ZnS from the complex. The resulting white solid gave analytical results suggesting the formation of ZnS. Anal. Calcd for ZnS: Zn, 67.1; C, 0.0; H, 0.0. Found: Zn, 66.0; C, 1.28; H, 0.40.

A 50-mL flask containing complex **4** (100 mg, 0.47 mmol) was sealed with a rubber septum. The system was evacuated with a syringe connected to a vacuum pump. After 8 h of heating at 260 °C, GC analyses of the gaseous and liquid products showed formation of propene (8%), 2-propanethiol (17%), and isopropyl sulfide (22%). Other hydrocarbons and isopropyl disulfide were not detected in the mixture. The remaining white solid contained 29 wt % carbon.

Kinetic Measurements. Complexes **1a** (13–17 mg), **1b** (7–8 mg), and **2** (15–20 mg) were placed in an aluminum cell for TG analysis. TG curves were recorded at constant temperatures under a nitrogen stream.

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