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COMPLEXES OF GROUP II_b METALS WITH DITHIOOXAMIDES. I. THERMAL PROPERTIES OF $Zn(CH_3NHCSCSNHCH_3)X_2$ (X = Cl, Br, I) COMPLEXES

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ABSTRACT

The thermal behaviour of the $Zn(NN'DMDTO)X_2$ (X = Cl, Br, I) complexes has been studied, using isothermal as well as non-isothermal techniques. The stable intermediate products are polymers, which contain terminal or bridging metal–halogen bonds, as confirmed by IR spectroscopy. The activation energy of the decomposition was determined by two methods, an isothermal method and the non-isothermal method of Flynn and Wall.

INTRODUCTION

Pellacani and coworkers [1] have determined the crystal-structure of $Zn(NN'DMDTO)Cl_2$. We recently proposed a thorough vibrational analysis of the $Zn(NN'DMDTO)X_2$ complexes by Cl/Br/I, $^{64}Zn/^{68}Zn$, NH/ND and CH_3/CD_3 substitution [2]. The complexes consist of discrete molecular units, interacting through hydrogen bonds between the halogen of one unit and hydrogen of the neighbour compound. The general structure of the complexes is given in Fig. 1. In this study the thermal behaviour of the complexes is presented.

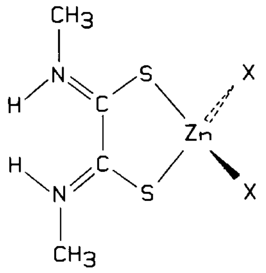

Fig. 1. The general structure of $Zn(NN'DMDTO)X_2$ (X = Cl, Br, I).

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EXPERIMENTAL

The thermogravimetric determinations were done using a Du Pont R90 thermal analyser, equipped with a 951 TGA Cahn Balance, in an N_2 atmosphere, with a flow rate of 50 ml min^{-1}.

Heating rates of 1, 5, 10 and 20 °C min^{-1} were used. The use of these four available heating rates on the R90 unit gives us more information about possible stable intermediates and about the activation energy, E_a, of the decomposition reactions. These calculations were carried out on an HP 1000 minicomputer.

DISCUSSION

The thermal decomposition curves of the $Zn(NN'DMDTO)X_2$ ($X = Cl$, Br, I) complexes are given in Fig. 2. All complexes are rather stable and start to decompose at about the same temperature.

The $Zn(LH_2)Cl_2$ complex shows a mass level for a stable intermediate at 64% and the $Zn(LH_2)Br_2$ and $Zn(LH_2)I_2$ complexes show an inflexion point in the curve in this region. The loss of mass at this point depends on the heating rate. The higher the heating rate, the higher the temperature of this point and the smaller the mass loss. This can be explained in terms of the decomposition of the "intermediate" itself. The best approach to prepare intermediates of these complexes is to heat them isothermally.

When the $Zn(LH_2)Br_2$ complex is heated for 20 h at a temperature of 180 °C, a fairly constant mass level is reached at about 61%. The $Zn(LH_2)I_2$ complex was heated isothermally at six different temperatures. There is a difference between the temperature in the oven tube (< programming unit) and at the sample point. The exact temperatures at this point, measured with a thermocouple, were used in the calculations.

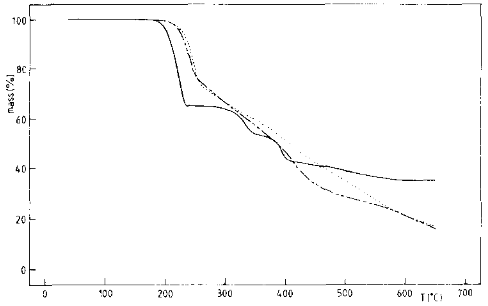


Fig. 2. Thermal decomposition curves of $Zn(NN'DMDTO)X_2$ (heating rate = 10 °C min^{-1}). ——— $X = Cl$; ······ $X = Br$; – – – – $X = I$

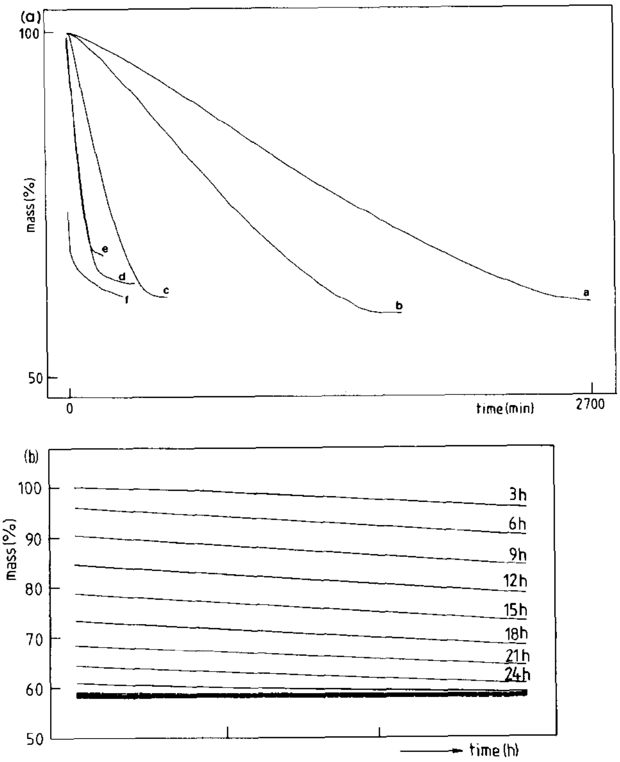


Fig. 3. (a) The decomposition curves of $Zn(NN'DMDTO)I_2$ at different temperatures (a = 167° C, b = 175° C, c = 191° C, d = 204° C, e = 206° C, f = 236° C) are obtained by digitization of an experimental decomposition curve. (b) The experimental decomposition curve for 175° C. The length of each line corresponds to a heating time of three hours, after which the pen moves back to the left side of the plotter.

The constant mass level is not exactly the same for the different temperatures and no correlation between temperature and mass level could be found (see Fig. 3 and Table 1).

When $(1-\alpha)$, where α is the decomposed fraction, is plotted as a function of time, the order of the reaction can be found. When the relation $(1-\alpha)$ vs. time is linear, the reaction is of zero order and when $\log(1-\alpha)$ vs. time is linear, the reaction is of the first order. In Fig. 4 the relations $(1-\alpha)$ vs. time and $\log(1-\alpha)$ vs. time are shown for the six different temperatures. Notice that for the three lower temperatures the reaction is of zero order and for the higher temperatures it is first order. For the two middle temperatures the correlation coefficients of the straight lines are smaller than for the four others, indicating a reaction order between zero and one.

Consider the following consecutive reactions

$$B \xrightarrow{k_1} B^{\star} \xrightarrow{k_2} E + V\uparrow$$

TABLE 1

Relation between temperature of decomposition and horizontal mass level of $Zn(NN'DMDTO)I_2$

Temperature (°C)	Mass level (%)
169	60
175	59
191	62
204	64
206	67.5
236	61

where B = starting material, $B^\star$ = activated complex, E = end product and V = volatile compounds. Then

$$\frac{d[B^\star]}{dt} = k_1[B] - k_2[B^\star]$$

where [B] = fraction of the remaining quantity B, and $[B^\star]$ = fraction of B in the activated form $B^\star$.

We cannot speak in terms of concentrations because we are dealing with solid state reactions. The kinetics and order of the total reactions are really those of the rate determining step, which is the slowest of the stages in that reaction. In the reaction at the three lower temperatures, k_2 is the rate determining step. This step is independent of [B] and gives rise to a zero-order reaction. At the higher temperatures, k_1 is the rate determining step and, being dependent on [B], it gives rise to a reaction of the first order.

If the three zero-order reactions are considered, the effect of the temperature on the reaction rate can be investigated. Using the Arrhenius equation, the following equation can be found

$$E_a = \ln\frac{k_2}{k_1} \cdot R \cdot \frac{T_1T_2}{T_2 - T_1}$$

From the experiment the equations for the three straight lines at the three different temperatures are derived. Knowing that the slope of the straight lines is proportional to the specific rate and inserting these values in the equation, E_a can be calculated three times: $E_a(169\,°C/175\,°C) = 135$ kJ mol^{-1}; $E_a(175\,°C/191\,°C) = 132$ kJ mol^{-1}; $E_a(169\,°C/191\,°C) = 133$ kJ mol^{-1}. The activation energy E_a of the decomposition reactions can also be determined with the variable heating rate method proposed by Flynn and Wall [3]. In this approach, the decomposition profiles of $Zn(NN'DMDTO)X_2$ (X = Cl, Br, I) are recorded at the four available heating rates. Temperatures at chosen decomposition levels are measured and are used to calculate E_a for each decomposition level. The average values of these activation energies are: $Zn(LH_2)Cl_2$: (133 ± 7) kJ mol^{-1}; $Zn(LH_2)Br_2$: (127 ± 1) kJ mol^{-1}; $Zn(LH_2)I_2$: (125 ± 8) kJ mol^{-1}.

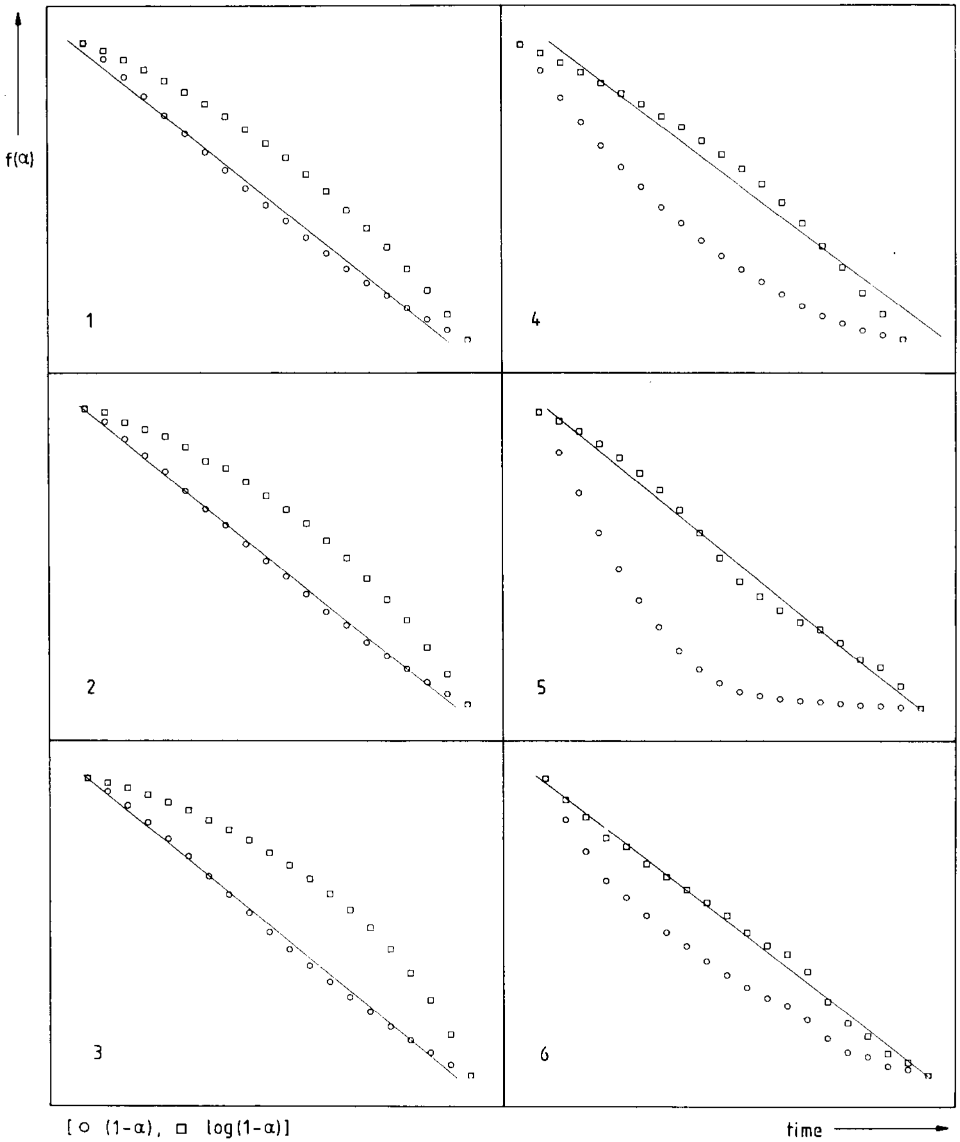


Fig. 4. Relations between the decomposed fraction and time.

In accordance with the results of Hofmans and coworkers [4,5] the following reaction is proposed

$$n\text{Zn(LH}_2\text{)X}_2 \xrightarrow{T\uparrow} (\text{ZnL})_n + 2n\text{HX}$$

However, experimentally the loss of ligand as well as the loss of HX was demonstrated. The ligand, which sublimated in the oven tube, was dissolved

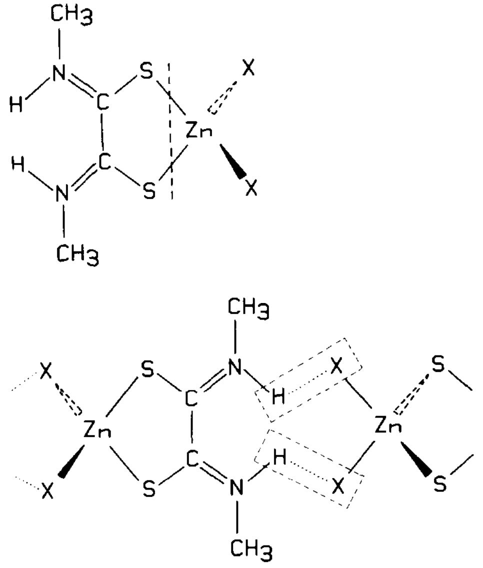


Fig. 5. The cleavage of the complex and the formation of HX + polymer respectively.

in methanol and determined by UV spectroscopy. The HX was collected in 1 ml water and the drop in pH of this solution was shown with a universal indicator. The precipitate which formed after addition of $AgNO_3$ indicated the presence of X^- ions. Therefore the most likely reaction is the following

$$x\mathrm{Zn(LH_2)X_2} \xrightarrow{T\uparrow} y\mathrm{HX} + z\mathrm{LH_2} + (\mathrm{ZnL})_{x-z}(\mathrm{ZnX_2})_{x-2y}$$

The mechanism is given in Fig. 5.

The MIR spectra of the intermediates are comparable with the spectra of the $(\mathrm{ZnL})_n$ deprotonated polymer, which was prepared in an alkaline alcohol solution [2]. One of the canonical forms of the proposed planar polymeric structure of $(\mathrm{ZnL})_n$ is given in Fig. 6 [5–7]. Notice the change of conformation between the complex and the polymer. In the FIR spectra there are a few differences between the different intermediates (see Table 2).

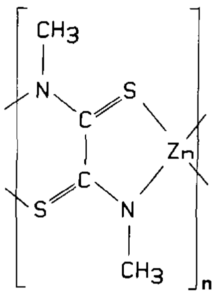
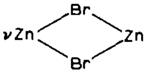
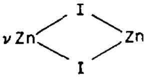


Fig. 6. One of the canonical forms of $[\mathrm{Zn(CH_3NCSCSNCH_3)}]_n$.

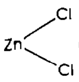
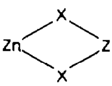
TABLE 2

FIR bands of the different polymers

Zn(NN'DMDTO) prepared in alkaline medium		$Zn(LH_2)Cl_2$ intermediate	$Zn(LH_2)Br_2$ intermediate	$Zn(LH_2)I_2$ intermediate	Assignment
^{64}Zn	^{68}Zn				
391 m	389 m	391 wm	393 wm	391 wm	νZn–N
		300 wvbr			νZnCl
273 m	271 m	271 wm	273 wm	270 wm	ν_{as}ZnS
	260 sh	260 sh	261 sh	254 wm	ν_sZnS
214 wm	214 wm		208 wm	201 wm	δNZnS
			168 m		
				142 m	
81 w	81 w		72 wm	69 wm	lattice

For the Cl-complex-intermediate, the extra broad band around 300 cm^{-1} is assigned to a terminal ZnCl vibration. For the Br-intermediate, an extra band appears at 168 cm^{-1}. In contrast to the Cl-intermediate, this band must be assigned to a bridged ZnBr vibration, according to the literature [8].

For the I-complex-intermediate, two extra bands appear. In accordance with the Br-intermediate, the band at 142 cm^{-1} can be assigned to a bridging ZnI mode. The band at 252 cm^{-1}, which appears as a shoulder in the spectra of the other "polymers", is assigned to a symmetric νZnS stretching mode.

The structure of the thermal polymers is probably three dimensional and consists of $(ZnL)_n$ and of terminal  or bridging  parts.

The different behaviours of the metal–halogen bonds of the polymers may explain why the intermediates of the Br- and I-complexes are less stable than the Cl-complex (i.e. inflexion point < > horizontal mass level in the TGA curve).

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