Journal of Thermal Analysis, Vol. 32 (1987) 91–96

STUDIES ON TRANSITION-METAL PICOLINE COMPLEXES

I. Preparation and thermoanalytical investigations

G. Liptay, A. Borbély-Kuszmann and *G. Nagy*

TECHNICAL UNIVERSITY, BUDAPEST, HUNGARY–1521; CENTRAL RESEARCH INSTITUTE FOR PHYSICS, BUDAPEST, HUNGARY–1525

(Received November 10, 1985)

A large number of transition-metal picoline halides were prepared, and their thermal decompositions were investigated by TG, DTG, DTA and thermomicroscopy. The compounds were classified on the basis of their thermal properties and two possible mechanisms of thermal decomposition were established.

The transition-metal halide complexes formed with pyridine and its derivatives have been studied intensively in recent years [1, 2]. Much attention has been paid to the metal picoline halides, which are of great interest in complex chemistry from a theoretical point of view and because of the possible analytical applications [3]. These complexes tend to form clathrates with a number of organic compounds, and are therefore of industrial importance, too [4].

A number of papers have reported on the decompositions of one or another transition-metal picoline halide and the kinetics of the process is well known [5]. However, the mechanism of the reaction and the classification of the complexes from this aspect have not yet been described.

We have prepared a large number of transition-metal picoline halides and studied them with a derivatograph and a thermomicroscope. In this paper we present the general conclusions of our thermoanalytical investigations and give a detailed discussion of our results.

Experimental

The preparation of the complexes is based on the reaction:

$$MX_2 + nL \rightarrow ML_nX_2 \tag{1}$$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

where M is a transition-metal, L is a picoline and X is a halide. The metal halide was dissolved and added to the picoline in an approximate molar ratio of 1 : 6. Water [6], ethanol [6], acetone [7] or even picoline [7] can be used as solvent. The reaction mixture was refluxed for an hour, when solid phase appeared. The mixture was then cooled, and the solid was filtered off and dried above $CaCl_2$ sicc. or under vacuum. If necessary, the initial metal halide was prepared [8] and the picoline was distilled in vacuum. The complexes listed in Table 1 were prepared with this method.

The thermoanalytical investigations were carried out with a MOM–G425 derivatograph. A sample weight of 100 mg was used and the heating rate was 5 deg/min. A N_2 atmosphere was applied in some cases, to avoid oxidation of the sample. A Boetius PHMK 05 thermomicroscope was used to visualize the processes.

Results

The compositions of the prepared complexes are seen in Table 1. It is worth mentioning that the complexes with α-picoline contain at most two ligands, because of the steric structure. Zinc dipicoline halides could be prepared with each of the picolines, because of the closed *d* shell of zinc.

The thermal decompositions of these transition-metal picoline halides can be described in general by the following equation:

$$ML_nX_2 \rightarrow MX_2 + nL \tag{2}$$

The process can be regarded as a consecutive reaction, as several steps were generally observed during the heating. In some cases, endothermic secondary

Table 1 Compositions of the prepared complexes (the data are the values of n in ML_nX_2)

	Ni	Co	Mn	Cd	Cu	Zn	
	2	2*	1	1	2*	2*	α-pic
Cl	4	4	4	2	2	2*	β-pic
	4	4	4	4	2.5	2*	γ-pic
	2	2*	1	2	2*	2*	α-pic
Br	4	4*	4	2	2	2*	β-pic
	4	4*	4	4	4	2*	γ-pic
	1	2*	1	2	—	2*	α-pic
I	4	4*	4*	2*	—	2*	β-pic
	6	4*	4*	4*	—	2*	γ-pic

* denotes members of the first group of complexes.

reactions occurred without any weight loss, as demonstrated by the DTA curves. These processes are presumed to involve structural change or phase transition. When these samples were examined with a thermomicroscope, it was possible to decide which of the two transitions took place.

The shapes of the TG and DTG curves and the stoichiometry of the thermal decomposition products permitted division of the complexes into two groups.

A. Melting during thermal decomposition

Typical representatives of the first group of complexes denoted by asterisks in Table 1, are $Co(\beta\text{-pic})_4Br_2$ and $Zn(\alpha\text{-pic})_2I_2$. Their thermal curves are shown in Fig. 1/a and Fig. 1/b. The first thermal decomposition step for the tetrapicoline complexes takes place in the solid phase and results in a dipicoline compound (Fig. 1/a), which is shown to melt by the endothermic DTA peak without weight loss (Fig. 1/a, b). The melting was also observed with the thermomicroscope. The melting points are collected in Table 2. Finally, two picolines leave together from the melt phase.

The overall reaction is described by the following equations:

$$ML_4X_2(s) \rightarrow ML_2X_2(s) + 2\,L(g) \qquad (3/a)$$

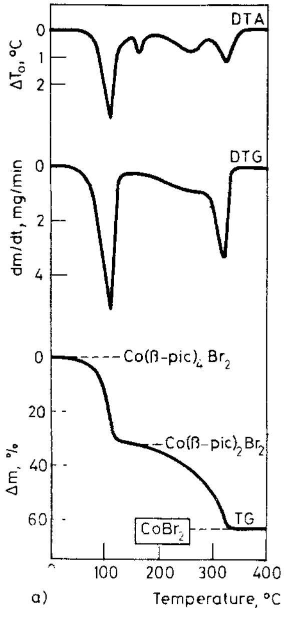

Fig. 1/a TG, DTG and DTA curves of $Co(\beta\text{-pic})_4Br_2$

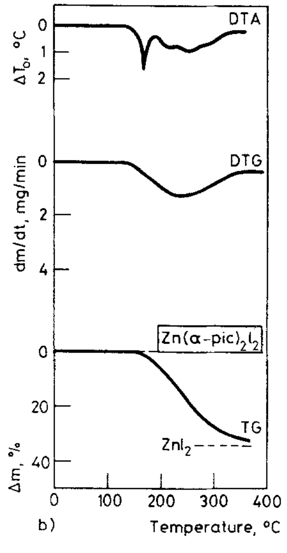

Fig. 1/b TG, DTG and DTA curves of $Zn(\alpha\text{-pic})_2I_2$

$$ML_2X_2(s) \rightarrow ML_2X_2(l) \qquad (3/b)$$

$$ML_2X_2(l) \rightarrow MX_2(s) + 2\,L(g) \qquad (3/c)$$

For the dipicoline halides, the first process (Eq. 3/a) is not relevant, and the zinc complexes, for instance, decompose in the melt phase according to Eqs 3/b and 3/c.

Table 2 Observed melting points, °C

	Ni	Co	Mn	Cd	Cu	Zn	
	—	142	—	—	145	155	α-pic
Cl	—	—	—	—	—	157	β-pic
	—	—	—	—	—	167	γ-pic
	—	156	—	—	138	147	α-pic
Br	—	163	—	—	—	179	β-pic
	—	138	—	—	—	154	γ-pic
	—	172	—	—	—	163	α-pic
I	—	173	95	87	—	167	β-pic
	—	131	145	110	—	159	γ-pic

B. Thermal decomposition in the solid phase

The compounds of the second group (without asterisks in Table 1) are characterized by various stoichiometries, but their thermal decompositions proceed in the same stepwise way in the solid phase. The reaction can be described generally by the following equations:

$$ML_4X_2(s) \rightarrow ML_2X_2(s) + 2\,L(g) \qquad (4/a)$$

$$ML_2X_2(s) \rightarrow ML_1X_2(s) + L(g) \qquad (4/b)$$

$$ML_1X_2(s) \rightarrow ML_nX_2(s) + (1-n)L(g) \qquad (4/c)$$

$$ML_nX_2(s) \rightarrow MX_2(s) + nL(g) \qquad (4/d)$$

The product formed in Eq. 4/c has a fractional ligand number; n is generally 2/3, but can be 1/2 or 1/3 in individual cases.

For the initial tetrapicoline complexes (Fig. 2/a), we found steps corresponding to Eqs 4/a–4/d. For the dipicoline halides, the first process (Eq. 4/a) is not involved (Fig. 2/b). When the initial compound contains only one ligand, the thermal decomposition is characterized by Eqs 4/c and 4/d (Fig. 2/c).

The DTG curve returns to the base line after every decomposition step, which proves that the intermediates formed are well-defined and of stoichiometric composition. These products can not be prepared from solution, but it is possible to

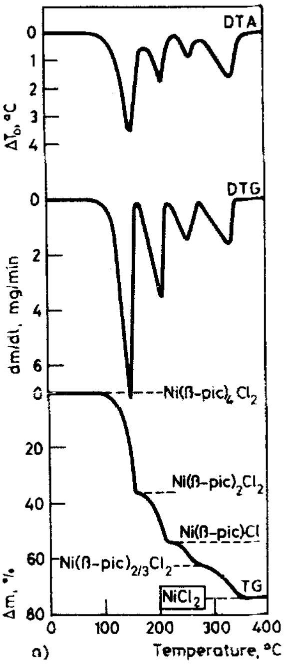

Fig. 2/a TG, DTG and DTA curves of Ni(β-pic)$_4$Cl$_2$

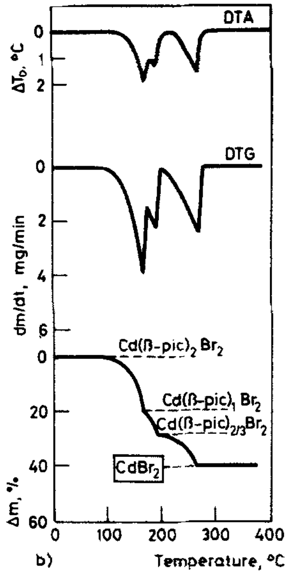

Fig. 2/b TG, DTG and DTA curves of Cd(β-pic)$_2$Br$_2$

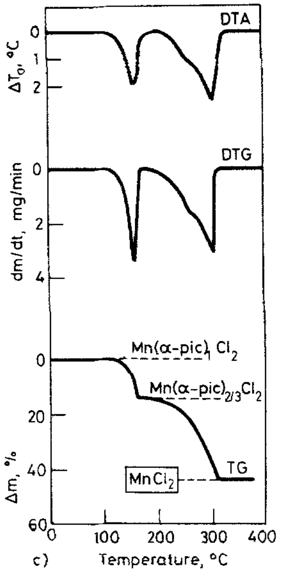

Fig. 2/c TG, DTG and DTA curves of Mn(α-pic)$_1$Cl$_2$

isolate them by means of the derivatograph, via freezing of the thermal decomposition at the appropriate temperature. This method is the only way to prepare the product of Eq. 4/c, which is interesting from a structural point of view. Because of their fractional stoichiometry, these compounds can be conceived as having a polynuclear structure. This assumption is supported by our structural investigations on the manganese picoline halides [9].

Conclusions

The picoline content of the complexes depends on different factors:

(a) the position of the methyl group on the pyridine ring; the ligand numbers of the complexes tend to increase in the sequence:

$$\alpha\text{-pic} < \beta\text{-pic} < \gamma\text{-pic}$$

(b) the electronic structure of the metal halide;

(c) the preparation method; the influence of this factor will be discussed in a subsequent paper.

The thermoanalytical investigations indicate a division of the complexes, depending on the stoichiometry of their thermal decomposition: Melting was observed during the thermal decomposition of the first group (denoted by asterisks in Table 1). Stepwise thermal decomposition was found for the second group, with the formation of well-defined intermediates. It is thought that the difference between the two mechanisms depends on the ionic character of the complexes and on the possibility of structural changes during thermal decomposition. This assumption will be returned to in a later paper.

References

1 G. Liptay, E. Papp-Molnár, Sz. Szebeni and F. Ruff, J. Inorg. Nucl. Chem., 31 (1969) 2359.

2 J. E. House and R. L. Rohner, Thermochim. Acta, 19 (1977) 119.

3 J. E. D. Davies and K. T. Holmes, J. Mol. Struct., 42 (1977) 59.

4 J. D. Jacobs and M. T. Lok, Inorg. Chem., 10 (1971) 1823.

5 E. Segal and D. Fatu, Introducere in Cinetica Neizoterma (Introduction in Non-isothermal Kinetics—in Roumanian), Editura Academiei, Republici Socialiste Romania, Bucuresti, 1983.

6 H. Langfelderova, L. Macaskova, M. Melnik and J. Gažo, Z. Anorg. Chem., 445 (1978) 214.

7 J. R. Allan, D. H. Brown and R. H. Nuttal, J. Chem. Soc., H8 (1966) 1031.

8 G. Brauer, Preparative Anorganische Chemie, Ferdinand Enke Verl., Stuttgart, 1962.

9 V. Izvekov, G. Liptay and G. Nagy, Spectroscopy Letters (in press).

Zusammenfassung — Zahlreiche Übergangsmetall-Picolin-Halide wurden dargestellt und deren thermische Zersetzung mittels TG, DTG, DTA und Thermomikroskopie untersucht. Die Verbindungen wurden nach ihren thermischen Eigenschaften klassifiziert, und zwei mögliche Mechanismen der thermischen Zersetzung sind angegeben.

Резюме — Получен ряд комплексов переходных металлов с пиколинами, термическое разложение которых изучено методами ТГ, ДТА, ДТГ и термомикроскопии. Классификация соединений проведена на основе их термических свойств и установлено два возможного механизма термического разложения.