

V. JORDANOVSKA and S. ALEKSOVSKA

### THERMAL DECOMPOSITION OF THE COMPLEXES OF SOME METAL OXALATES WITH PYRIDINE

The thermal decomposition of  $\text{FeC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ ,  $\text{CoC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  and  $\text{ZnC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  was studied, by thermogravimetry and differential thermal analysis, in air-flow, in a temperature range from 20 to 700°C, with a heating rate of 10°C/min.

From the X-ray powder diffraction patterns and the percentage of the residue of the thermal decomposition, it can be concluded that in the air atmosphere the thermal decomposition of  $\text{ZnC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  goes to  $\text{ZnO}^\dagger$  of  $\text{FeC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  to  $\text{Fe}_2\text{O}_3$ , and of  $\text{CoC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  to  $\text{Co}_3\text{O}_4$ .

#### Introduction

A survey of the literature shows that metal oxalate complexes with alifatic and aromatic amines have been extensively studied. There are also some data on the pyridine complexes of some transition metal oxalates. The crystal structures of bis(pyridine)cobalt(II) oxalate and bis(pyridine)nickel(II) oxalate are already known [1], and the infrared spectra of bis(pyridine)cobalt(II) oxalate have been studied too [2].

However, the thermal decomposition of pyridine complexes of the transition metal oxalates has not been completely studied. There are some data about the thermal decomposition of  $\text{CuC}_2\text{O}_4 \cdot \text{C}_5\text{H}_5\text{N}$  [3], and of  $\text{CoC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  to 400°C [4].

In an attempt to determine some relationships between the structures of the complexes and the course of their thermal decomposition, we present in this paper the results of a thermal analysis of  $\text{MC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  (where M is  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$ )

#### Experimental procedure

Complexes with empirical formula  $\text{MC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  (where M is  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$ ), were obtained by a treatment of freshly prepared metal oxalates with an excess of pyridine. The metal oxalates were prepared from a mixture of aqueous solutions of the corresponding metal sulfates and oxalic acid.

The pyridine complexes were synthesized by refluxion of the reaction mixture of the corresponding metal oxalate and pyridine for two hours. The obtained compounds were then filtered off, dried in air and identified and investigated by the methods of X-ray powder diffraction, TG and DTA analysis and elemental analysis.

#### *Apparatus and methods*

The X-ray powder diffraction patterns were obtained on a JEOL-diffractometer, model JDX-7E with Cu-K $\alpha$ -radiation, Ni-filtered.

TG and DTA curves were obtained on a NETZSCH thermoanalyser, in a flow of dry air. Experimental conditions: reference substance for DTA determination  $\alpha$ -Al $_2$ O $_3$ , heating rate 10°C/min, temperature range 20—700°C.

The metal was determined by complexometric titration with EDTA, and oxalate anion by permanganometric titration.

#### *Results and discussion*

The results of the elemental analysis of the obtained compounds (Table I) show that they have the empirical formula MC $_2$ O $_4$ ·2C $_5$ H $_5$ N.

Table I

*Results of the elemental analysis of MC $_2$ O $_4$ ·2C $_5$ H $_5$ N (M = Zn $^{2+}$ , Fe $^{2+}$ , Co $^{2+}$ )*

	Zn		Fe		Co	
	theor.	exp.	theor.	exp.	theor.	exp.
%C	46.25	45.92	47.71	46.93	47.23	46.48
%H	3.23	3.80	3.33	3.72	3.27	3.78
%N	8.99	9.45	9.27	9.34	9.18	10.01
%M $^{2+}$	20.98	20.83	18.48	18.29	19.31	18.84
%C $_2$ O $_4^{2-}$	28.24	28.03	29.13	30.09	28.83	28.00

The X-ray powder diffraction patterns of the obtained compounds (Fig. 1) show that they are not isostructural, although the X-ray powder diffraction patterns of the metal oxalates are isostructural. Therefore, it was of interest to study the thermal behaviour and to correlate the structure with the mechanism of the thermal decomposition.

TG and DTA curves of the obtained compounds are given in Fig. 2 (a, b, c).

The thermal decomposition of bis(pyridine)zinc oxalate takes place in three stages (Fig. 2-a). In the first stage of decomposition, the complex loses one molecule of pyridine in the temperature range from 165—250°C (calculated values 25.37%, found 25.34%), which is followed by an endothermic peak at 205°C.

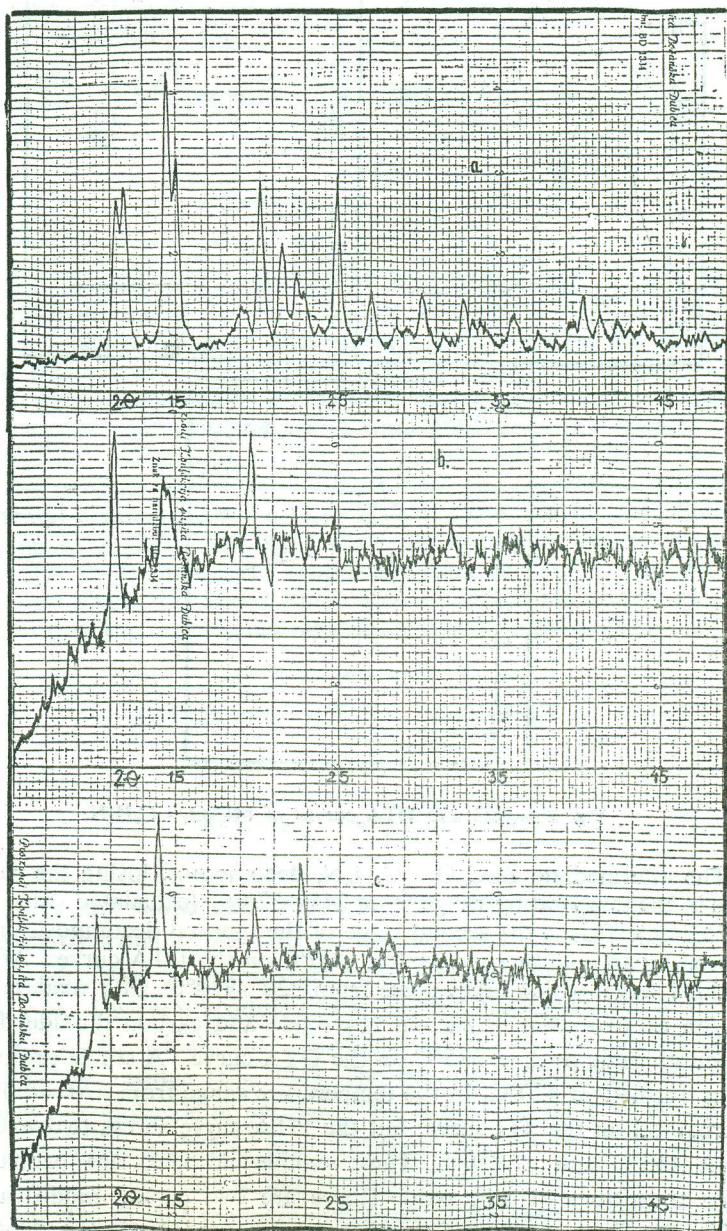


Fig. 1 — The X-ray powder diffraction patterns of  $MC_2O_4 \cdot 2C_5H_5N$

(a: M = Zn; b: M = Fe; c: M = Co)

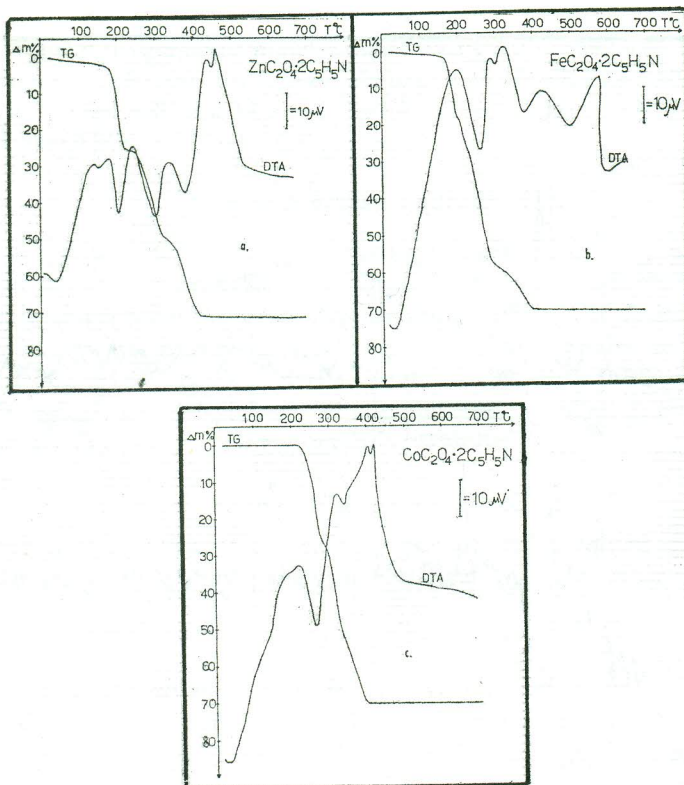
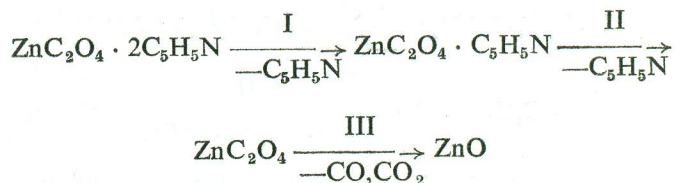


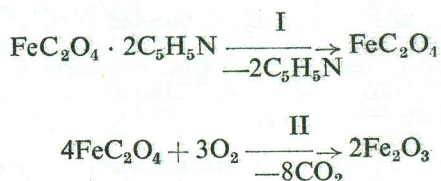
Fig. 2 — TG and DTA curves of  $\text{MC}_2\text{O}_4 \cdot \text{C}_5\text{H}_5\text{N}$

The intermediate  $\text{ZnC}_2\text{O}_4 \cdot \text{C}_5\text{H}_5\text{N}$ , decomposes, losing the remaining pyridine in the temperature range from 245–320 $^{\circ}\text{C}$  (calculated value 25.37%, found 25.24%). This is the second stage of the thermal decomposition, which is followed by an endothermic peak at 300 $^{\circ}\text{C}$  on the DTA curve. After that, in the third stage, which takes place from 320–420 $^{\circ}\text{C}$ , zinc oxalate decomposes with an evolution of carbon monoxide and carbon dioxide, followed by an endothermic peak at 385 $^{\circ}\text{C}$  on the DTA curve. A stable product, zinc oxide, is formed at 420 $^{\circ}\text{C}$ . In the temperature range from 420–700 $^{\circ}\text{C}$  there is a horizontal on the TG curve, but the DTA curve shows two exothermic peaks at 440 $^{\circ}\text{C}$  and at 450 $^{\circ}\text{C}$ . These exothermic peaks are probably due to phase transitions of zinc oxide (there are two crystal modifications of ZnO) [5]. The final product of the thermal decomposition was identified by X-ray powder diffraction patterns of the residue (Fig 3-a), and from the theoretical values and experimental results (theor. ZnO 26.10%, residue of thermal decomposition 27.62%).

In general, the thermal decomposition of bis(pyridine)zinc oxalate can be expressed as:

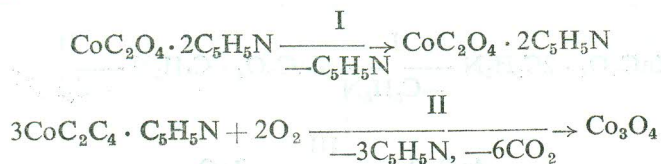


The thermal decomposition of bis(pyridine)iron oxalate (Fig. 2-b) is different from that of the zinc complex. It begins at 170°C and is complete at 400°C, when a stable product appears (horizontal on the TG curve). In this case, it is not possible to identify  $\text{FeC}_2\text{O}_4 \cdot \text{C}_5\text{H}_5\text{N}$ , so it can be concluded that both pyridine molecules are involved in one step, which is followed with an endothermic peak at 260°C. The final product of the thermal decomposition is  $\text{Fe}_2\text{O}_3$  (Fig. 3-b), which was concluded by the X-ray powder diffraction patterns of the residue and from the theoretical calculated and experimental results (theor.  $\text{Fe}_2\text{O}_3$ —26.42%, exper. 29.34%). In the temperature range from 400°C to 700°C, there is a horizontal on the TG curve, but on the DTA curve there is an exothermic peak at 595°C. This peak can be due to some phase transitions (there are five crystal modifications of  $\text{Fe}_2\text{O}_3$ ) [5]. In this case the thermal decomposition can be expressed as:



There are some data about the thermal decomposition of bis(pyridine)cobalt(II) oxalate, but only in the temperature range from 20–400°C [4]. In this case it was studied in the temperature range from 20–700°C (Fig. 2-c). The final product of the thermal decomposition at this temperature is  $\text{Co}_3\text{O}_4$ , which was concluded by the X-ray powder diffraction patterns of the residue (Fig. 2-c). The decomposition begins at 220°C, with the loss of one molecule of pyridine. This is the first stage of decomposition, which is complete at 285°C (an inflection point on the TG curve). In the second stage of the thermal decomposition, which begins at 285°C and is complete at 390°C, the remaining molecule of pyridine is lost and the oxalate ion is decomposed. On the DTA curve this is followed by an endothermic peak at 265°C. There are also exothermic peaks at 405°C and at 410°C, which are probably due to formation of  $\text{Co}_3\text{O}_4$  [5].

The thermal decomposition of the cobaltous complex can be expressed as:



From all these results, it can be concluded that, although there are differences in the structure of the investigated compounds, the thermal decomposition is similar, but not quite the same. The thermal analysis shows

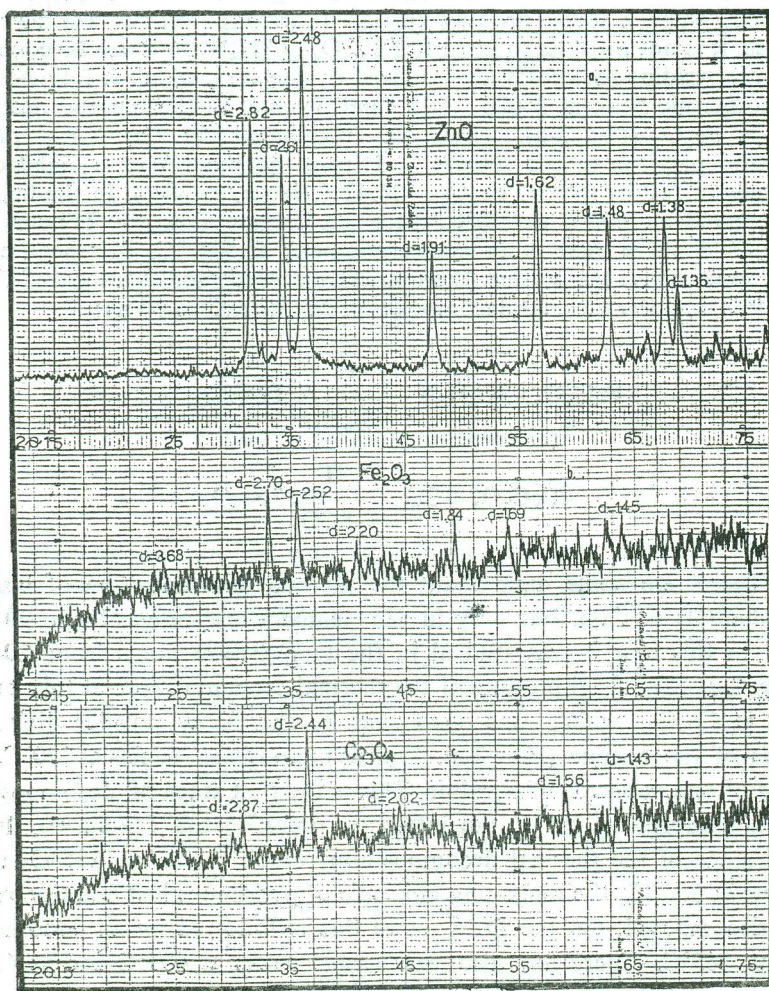


Fig. 3 — The X-ray powder diffraction patterns of the residues

that the cobaltous complex is the most stable, because its decomposition begins at the highest temperature in comparison with those of zinc complex and iron complex. Also, the iron complex loses both pyridine molecules in one step, but the zinc and the cobaltous complex loses the pyridine molecules step by step. It suggests that, probably, in the iron complex both pyridine molecules are bound in the same way.

## REFERENCES

- [1] S. K. Srivatsava, S. Sarkar, R. C. Manrya, B. Sharma, A. C. Nigan, R. K. Shukla, *Acta Scienc. Indica*, (Ser. Chem.), 5 (3), 113 (1979).
- [2] G. P. Singh, P. R. Shukla, L. N. Srivatsava, *J. Inorg. Nucl. Chem.*, 34 (10), 3251 (1972).
- [3] P. C. Srivatsava, B. N. Singh, S. D. Adhya and K. C. Benerji, *J. Therm. Anal.*, 27, 263 (1983).
- [4] W. W. Wendlandt and S. Iftikhar Ali, *Allgem. Chem.*, 337 (1-2), 6 (1965).
- [5] Inorganic index to the powder diffraction file (1972).

V. ЈОРДАНОВСКА и С. АЛЕКСОВСКА

ТЕРМИЧКО РАЗЛОЖУВАЊЕ НА КОМПЛЕКС  
МЕТАЛНИ ОКСАЛАТИ СО ПИРИДИН

(Резиме)

Термичкото разложување на  $\text{FeC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ ,  $\text{CoC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  и  $\text{ZnC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  беше испитувано со методите на термогравиметрија и диференцијална термичка анализа, во струја на воздух, во температурен интервал од 20—700°C, со брзина на загревање 10°C/min.

Според снимените рендгенски дифрактограми на остатоците од термичката анализа и според нивниот процент, може да се заклучи дека во атмосфера на воздух разложувањето на  $\text{ZnC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  се одвива до  $\text{ZnO}$ , на  $\text{FeC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  до  $\text{Fe}_2\text{O}_3$ , а на  $\text{CoC}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  до  $\text{Co}_3\text{O}_4$ .

*Institute of Chemistry, Faculty of Sciences,  
University "Kiril and Metodij",  
91000 Skopje.*