

## **SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF THE PYRIDINE ADDUCTS OF Co, Ni, Cu AND Zn SULFATE**

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### **Abstract**

Pyridine adducts of Co, Ni, Cu and Zn sulfate were obtained by refluxing the corresponding sulfate with pyridine in chloroform. The compounds were characterized by elemental analysis, X-ray powder diffraction and FTIR spectroscopy. The thermal decompositions (TG/DTG/DTA) of the complexes in the interval 20–1000°C were also studied.

The elemental and thermal analysis results revealed that the formulae of the complexes are  $M_2(SO_4)_2 \cdot xC_5H_5N_y \cdot H_2O$ , where  $x=2, 3, 2$  and  $1$  and  $y=6, 4, 6$  and  $4$  for the Co, Ni, Cu and Zn compound, respectively. The complexes were not found to be isostructural, but certain structural similarities were observed between the Zn and Co compounds. Although the thermal decomposition pathways of the various compounds were quite different and each consisted of several steps, in all cases the dehydration preceded the depyridination. Metal oxide was always obtained as final product.

The spectral data are discussed with regard to the thermal behaviour. Appreciably strong hydrogen-bonding and pronounced structural differences relating to the sulfate ions were presumed for the Cu compound.

**Keywords:** M(II) sulfates, pyridine adducts, thermal decomposition

### **Introduction**

For several decades, the thermal behavior of the pyridine adducts of various transition metal(II) salts, such as the halides, nitrates and thiocyanates, has been extensively studied and is well known [1, 2]. We earlier investigated the thermal decompositions of Fe, Co and Zn oxalates with pyridine [3].

A literature survey revealed, however, that data on the complexes of metal(II) sulfates with aromatic N-bases are rather scarce [4]. As concerns the complexes of pyridine with sulfate salts, only structural [5] and thermal data [6] for the Cu(II) adduct could be found. The compound was obtained by slow evaporation of an aque-

ous solution of Cu(II) sulfate and pyridine. The corresponding formula was found to be  $\text{Cu}(\text{py})_2(\text{H}_2\text{O})_2\text{SO}_4$  (py denotes the pyridine molecule). Its thermal behavior was studied and the experimental activation energy of dehydration was estimated [6]. The thermal decompositions of the complexes of Co(II) sulfate with 3-cyanopyridine and 4-cyanopyridine, of general formula  $\text{Co}(\text{cypy})_2\text{SO}_4$  (cypy denotes 3-cyanopyridine or 4-cyanopyridine), were also reported previously [7].

In the present paper, we report on the preparation and thermal decompositions of the pyridine adducts of Co, Ni, Cu and Zn sulfate. Their thermal behaviour was studied in the temperature interval from ambient up to about 1000°C in static air atmosphere. The complexes were additionally characterized via their powder diffraction patterns. In an attempt to predict certain structural characteristics, the main bands in their FTIR spectra were assigned and are discussed.

## Experimental

### *Preparation of the complexes*

Each of the complexes was prepared by the addition of dry pyridine (5 mL) to a solution of the corresponding powder hydrated metal(II) sulfate (0.005 mol) in chloroform (20 mL). The resulting mixture was refluxed for 3.5 h. The solid residue was filtered off and dried in air. The compounds proved stable at ambient temperature.

### *Analytical methods*

DTA and TG studies were carried out on a Q Derivatograph (MOM, Hungary) in a static air atmosphere in the temperature range from 293 to approximately 1273 K. The sample size was 100 mg;  $\beta=10 \text{ K min}^{-1}$  and Pt crucibles were used.

X-ray diffraction patterns were obtained with a TUR-M62 instrument (Dresden, Germany), using  $\text{CoK}_\alpha$  radiation and an iron target.

The spectra were recorded with a System 2000 FTIR spectrometer (Perkin Elmer) in the region 4000–400  $\text{cm}^{-1}$  as Nujol mull solid samples between KBr discs.

Elemental analysis of carbon and hydrogen were carried out on a Coleman model 33 instrument by the Liebig method, and nitrogen contents were determined by the Dumas method.

## Results and discussion

From the results of the elemental analyses, the water and pyridine contents and the residues from the TG analyses (Table 1), it follows that the compounds display varying stoichiometry, which can best be described by the general formula  $\text{M}_2(\text{SO}_4)_2 \cdot x\text{C}_5\text{H}_5\text{N}_y\text{H}_2\text{O}$ , where  $x=2, 3, 2$  and  $1$  and  $y=6, 4, 6$  and  $4$  for the Co, Ni, Cu and Zn compound, respectively.

X-ray powder diffraction patterns of the compounds are shown in Figs 1 and 2. Although the diffractograms of the compounds differ, there are some similarities be-

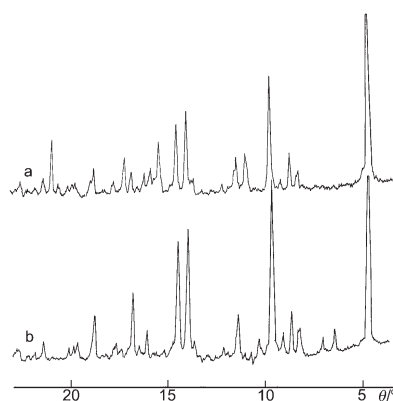
tween those of the Co and Zn compounds (Fig. 1). At the same time, these differ considerably from the X-ray patterns of the Cu and Ni compounds (Fig. 2).

**Table 1** Results of elemental and TG analyses of Co, Ni, Cu and Zn pyridine sulfates\*

Compound	C/	H/	N/	H <sub>2</sub> O/	py/	Residue/
	mass%					
CoSO <sub>4</sub> py·3H <sub>2</sub> O	20.1 (20.84)	3.6 (3.85)	4.6 (4.86)	45.5** (18.76)	(27.45)	28.4 (27.85)
Ni <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·3py·4H <sub>2</sub> O	30.0 (29.12)	4.1 (3.75)	6.2 (6.79)	11.7 (11.64)	37.8 (38.34)	24.4 (24.14)
CuSO <sub>4</sub> py·3H <sub>2</sub> O	19.4 (20.51)	4.5 (3.79)	5.3 (4.78)	45.9** (18.46)	(27.02)	26.2 (27.17)
Zn <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·py·4H <sub>2</sub> O	13.5 (12.67)	2.7 (2.76)	2.6 (2.95)	14.8 (15.20)	17.0 (16.69)	33.4 (34.32)

\*The asterisks denote the values of the mass loss for dehydration together with depyridination

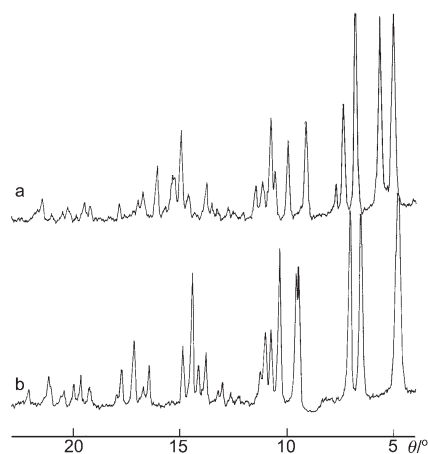
\*\*The numbers in brackets refer to the calculated values



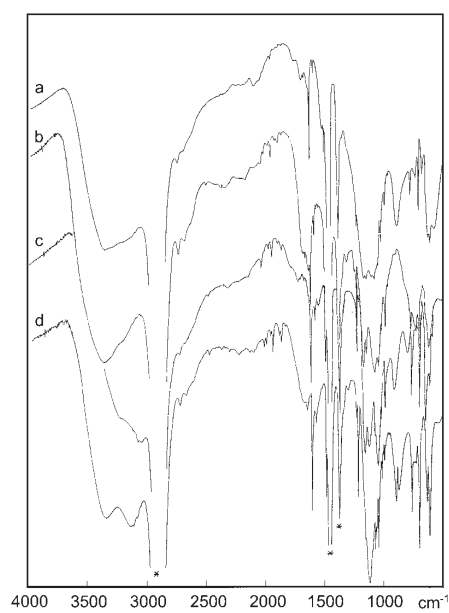
**Fig. 1** X-ray diffraction patterns of Co (a) and Zn (b) pyridine sulfate

### *Infrared spectra*

The FTIR spectra of the compounds are shown in Fig. 3. In general, the spectra of the Co and Zn compounds seem somewhat similar, but at the same time different from those of the Cu and Ni compounds. The bands in the region 3000–3500 cm<sup>-1</sup> are ascribed to the stretching modes, while the moderately intense and broad bands at around or somewhat lower than 1700 cm<sup>-1</sup> can be assigned as the bending mode of the water molecules. The markedly low frequency of the former (3048 cm<sup>-1</sup>) and the high frequency of the latter (1680 cm<sup>-1</sup>) for the Cu compound as compared with the other compounds lead to the conclusion of the pronounced strength of the hydrogen-bonding present in its structure. The sharp and strong bands at around 1600,



**Fig. 2** X-ray diffraction patterns of Cu (a) and Ni (b) pyridine sulfate



**Fig. 3** FTIR spectra of Zn (a), Co (b), Cu (c) and Ni (d) pyridine sulfate

1205, 775 and 605  $\text{cm}^{-1}$  belong to the benzenoid vibrational modes of the pyridine ring [8, 9]. The frequency shift of the band at around 1600  $\text{cm}^{-1}$  relative to the corresponding band in the spectrum of pyridine itself (1581  $\text{cm}^{-1}$  [9]) confirms the coordination of pyridine in these complexes. The sharp, strong bands at around 1100  $\text{cm}^{-1}$  can be assigned to the stretching mode of the sulfate groups. The splitting of this mode for the Zn, Co and Cu compounds can be explained in terms of rather distorted

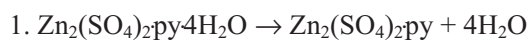
or structurally different sulfate groups [10]. The possibility of involvement in hydrogen-bonding and coupling effects can not be excluded. The sulfate groups in the Ni compound, however, are expected to be more uniform.

#### *Thermal data*

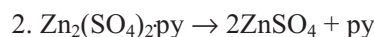
Besides the estimated differences in stoichiometry, and in the diffraction and IR data, which imply different structures for the title compounds, their thermal decompositions take place in a different way. It is most convenient, therefore, to discuss the thermal decomposition of each compound separately.

#### $Zn_2(SO_4)_2 \cdot py \cdot 4H_2O$

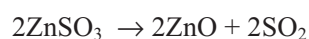
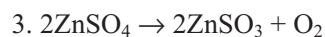
The thermal decomposition of  $Zn_2(SO_4)_2 \cdot py \cdot 4H_2O$  (Fig. 4) takes place in three well-differentiated stages. In the first stage of the decomposition, from ambient temperature up to 120°C, dehydration of the compound takes place. In the second stage, from 220 to 320°C, depyridination occurs, accompanied by two DTG peaks. In the last stage, from 680 to about 930°C, the decomposition of zinc sulfate takes place. This stage, however, could be thought of as composed of two consecutive processes. As may be seen from the DTA curve (Fig. 4), these processes are accompanied by two endothermic effects. The two consecutive steps may be ascribed to stepwise decomposition of the sulfate to sulfite and finally to oxide, as observed in some previous cases [11]. Thus, the thermal decomposition of the pyridine adduct of zinc sulfate could be expressed as follows:



(mass loss found: 15.0%, calculated: 15.20%)



(mass loss found: 18.0%, calculated: 16.69%)



(mass loss found: 33.6%, calculated: 33.78%)

#### $CoSO_4 \cdot py \cdot 3H_2O$

The thermal decomposition of  $CoSO_4 \cdot py \cdot 3H_2O$  proceeds in three steps (Fig. 5). The first and second steps, which partially overlap, correspond to dehydration and depyridination of the compound, respectively. It proved very difficult to distinguish the mass losses for each step separately. On the basis of the temperature corresponding to the minimum in the DTA curve (Fig. 5) and the temperature of the maximum in the DTG curve, the temperature interval for the first step can be estimated approximately. The overall mass loss for these two processes is 45.5%, which is close to the

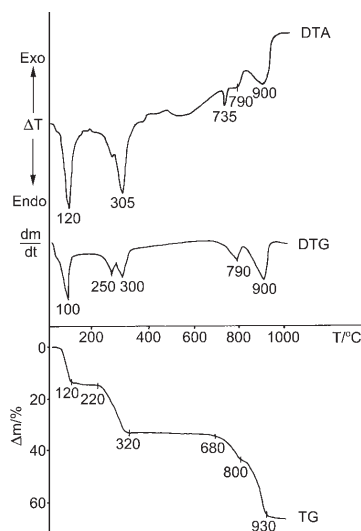
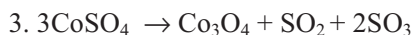


Fig. 4 TG, DTG and DTA curves of the thermal decomposition of Zn pyridine sulfate

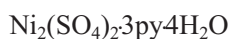
calculated value (46.20%). From 310 to 720°C, the TG curve is horizontal. A diffuse exothermic peak in the temperature interval from 300 to about 400°C in the DTA curve can be explained as due to stabilization of the molecular structure. In the third step, decomposition of  $\text{CoSO}_4$  to  $\text{Co}_3\text{O}_4$  takes place. This complex redox process, accompanied by dissociation, is accompanied by two endothermic peaks in the DTA curve (at 880 and 905°C):



(mass loss found: 45.5%, calculated: 46.20%)



(mass loss found: 26.1%, calculated: 25.93%)



The thermal decomposition of  $\text{Ni}_2(\text{SO}_4)_2\cdot 3\text{py}\cdot 4\text{H}_2\text{O}$  (Fig. 6) can be divided into three stages. Dehydration of the compound occurs in the first stage. In the second stage, however, the stepwise depyridination and dissociation of the nickel(II) sulfate to the corresponding sulfite can not be well resolved. In the third stage, decomposition of the remaining sulfite to oxide proceeds.

The first stage (from 80°C) and the second stage (up to 530°C) are not well differentiated. The temperature intervals corresponding to these processes, however, were successfully estimated by taking into account the inflection point at 165°C. The dehydration (the first step) is accompanied by an endothermic peak at 165°C (DTA curve) and a DTG peak at 155°C (Fig. 6). The depyridination in the second stage, on

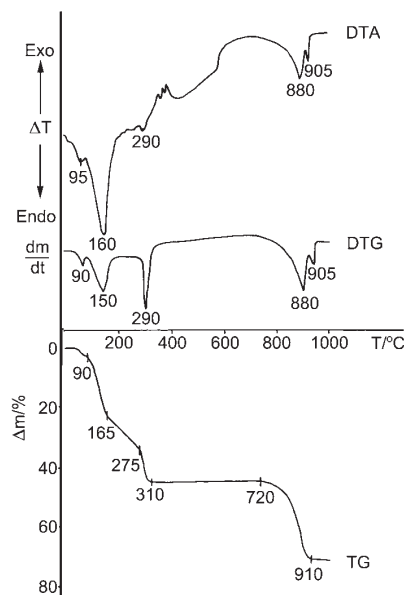
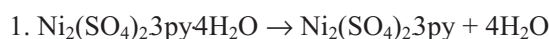
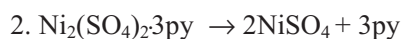


Fig. 5 TG, DTG and DTA curves of the thermal decomposition of Co pyridine sulfate

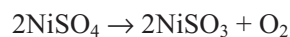
the other hand, takes place in two consecutive processes, accompanied by the appearance of two peaks in the DTG curve (at 220 and 345°C). Two endothermic peaks in the DTA curve (one at 225°C and the other a broad one at somewhat higher temperature) correspond to these processes. The depyridination therefore proceeds in a step-wise manner. The endothermic peak at 445°C (the DTA curve) accompanied by a small mass loss (the TG curve) is possibly due (as in the case of the Zn compound) to the decomposition of nickel sulfate to the corresponding sulfite (the theoretical value for the mass loss is 5.17%; found 4.5%). The lack of oxygen in the atmosphere prior to this process could be one of the possible factors that would favour this reaction. In the third stage, the decomposition of  $\text{NiSO}_3$  to  $\text{NiO}$  and  $\text{SO}_2$  takes place. Single DTA and DTG peaks at the same temperature (810°C) correspond to this stage:



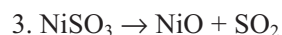
(mass loss found: 11.7%, calculated: 11.64%)



(mass loss found: 37.8%, calculated: 38.34%)



(mass loss found: 4.5%, calculated: 5.17%)



(mass loss found: 21.6%, calculated: 20.68%)

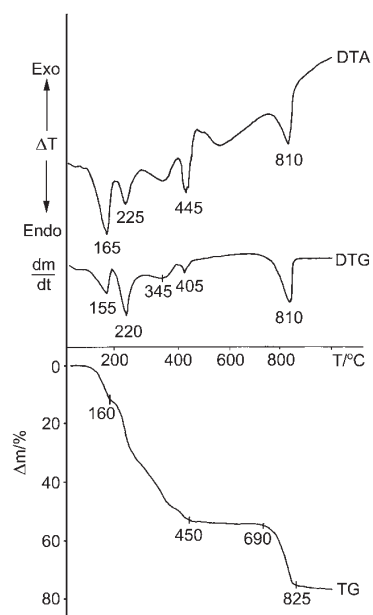


Fig. 6 TG, DTG and DTA curves of the thermal decomposition of Ni pyridine sulfate

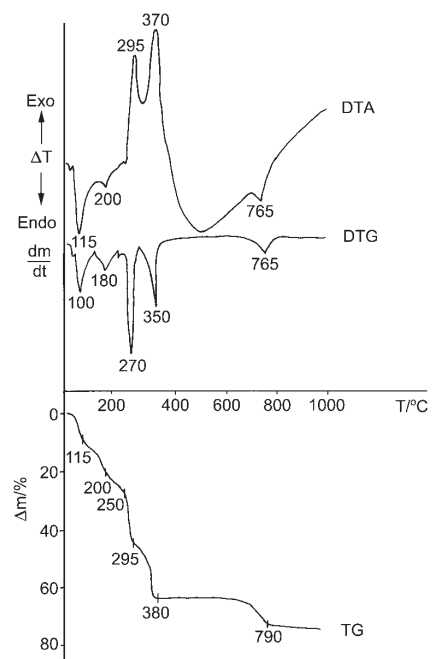
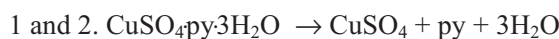


Fig. 7 TG, DTG and DTA curves of the thermal decomposition of Cu pyridine sulfate

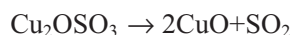


### CuSO<sub>4</sub>py·3H<sub>2</sub>O

The thermal decomposition of CuSO<sub>4</sub>py·3H<sub>2</sub>O (Fig. 7) is very complex and proceeds in many steps. Several of them overlap, and it is therefore very difficult to estimate the temperature intervals in which definite compounds exist. In the first step, from ambient up to about 130°C, as inferred from the thermoanalytical curves shown in Fig. 7, partial dehydration of the complex takes place. In the second step, the remaining water and the pyridine are lost. This is accompanied by an exothermic peak in the DTA curve and by two peaks (at 180 and 270°C) in the DTG curve. The dissociation of CuSO<sub>4</sub> in the third step, however, is rather complex. We presume for this process that the pyridine might be oxidized by oxygen resulting from the decomposition of CuSO<sub>4</sub>, which, on the other hand, proceeds at relatively low temperature. CuO is obtained as the final product:



(mass loss found: 45.9%, calculated: 45.48%)



(mass loss found: 27.9%, calculated: 27.35%)

## Conclusions

It is concluded as a common feature for the pyridine adducts of Co, Ni, Cu and Zn sulfate that the dehydration precedes the depyridination. With the exception of the Zn compound, these two processes overlap (for the Co and Cu compounds) or the temperature interval that separates them is very small (the Ni compound). It follows from the TG study that the Co and Ni compounds are more stable (with respect to the water of hydration) than the other two compounds. Despite the similarity of the IR spectra and the X-ray patterns of the Co and Zn compounds, their thermal decompositions exhibit rather different pathways.

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