

The thermal decomposition of the pyridine saccharinates of Co, Ni and Cu: A correlation of the structural and the infrared data

PANČE NAUMOV^{1*}, GLIGOR JOVANOVSKI,¹ VERA JORDANOVSKA¹ and
BOYAN BOYANOV²

¹*Institute of Chemistry, Faculty of Science, "Sv. Kiril i Metodij" University, P.O.Box 162, 91001
Skopje, Macedonia and*

²*Faculty of Chemistry, Plovdiv University, Paisii Hilendarski, 4025 Plovdiv, Bulgaria*

(Received 16 February 1999)

In order to investigate the differences in the stability of the isomorphous pyridine saccharinates $[\text{Co}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$, their thermal behavior (TG, DTG and DTA curves) from ambient temperature up to 1000 °C in a static air atmosphere was studied. For comparative purposes, the thermoanalytical curves of $[\text{Cu}(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$ were recorded as well. The decomposition pathways and the stability of the compounds are interpreted in the terms of the structural data. A possible mechanism for the decomposition of the saccharinato ion/ligand in an oxidizing atmosphere is proposed. The infrared spectral characteristics of the complexes are also discussed.

Key words: thermal decomposition, pyridine complexes, saccharinates, structure, infrared spectra.

Due to the common use of saccharin [systematic name: 1,2-benzisothiazole-3(2*H*)-one 1,1-dioxide] as a food additive and its suspected carcinogenic nature,¹ the structural properties of its salts and complexes with various metals have been extensively studied during the last two decades. Lately, however, scientific attention in this field has been focused on the adducts of saccharinates with ring nitrogen bases. It seems reasonable to suppose, namely, that the incorporation of such ligands in the saccharinato compounds might influence their physiological properties. However, except for some V(II)² and Zn(II)³ compounds, no detailed structural data could be found about saccharinato adducts with pyridine. In a continuation of our systematic study on metal saccharinates, we have recently determined the crystal structures of the compounds: $[\text{M}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$,⁴ $[\text{Cu}(\text{H}_2\text{O})(\text{py})_2(\text{sac})_2]$ ⁵ and $[\text{HgCl}(\text{py})(\text{sac})]_2$ ⁶ (hereafter M denotes Co or Ni, py stands for pyridine and sac is used to denote the saccharinato ligand or an ion).

* Author for correspondence, e-mail: spance@iunona.pmf.ukim.edu.mk

There are, on the other hand, some published thermal data on the pyridine saccharinates characterized as $\text{Co}(\text{py})_2(\text{sac})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{py})(\text{sac})_2 \cdot 4\text{H}_2\text{O}$,⁷ $\text{Ni}(\text{py})_2(\text{sac})_2 \cdot 8\text{H}_2\text{O}$,⁸ $\text{Ni}(\text{py})_3(\text{sac})_2 \cdot 2\text{H}_2\text{O}$,⁹ $\text{Cu}(\text{py})(\text{sac})_2 \cdot \text{H}_2\text{O}$,^{7,9} $\text{Cu}(\text{py})_2(\text{sac})_2 \cdot 2\text{H}_2\text{O}$,⁷ $\text{Zn}(\text{py})_2(\text{sac})_2 \cdot \text{H}_2\text{O}$ ⁸ and $\text{Zn}(\text{py})_2(\text{sac})_2$.³ However, the interpretation of the thermal decomposition of the nickel⁸ and the copper^{7,9} compounds, with formulae corresponding to those found by our crystal structure determination, seems rather doubtful. As it has been shown,^{4,5} most of the previous structural inferences deduced from thermal data,^{7,8} such as those concerning the number of nonequivalent water and pyridine molecules* or saccharinato ligands, as well as the participation of the saccharinato ligands in the coordination around the metal atom, are incorrect. Moreover, no explanation for the decomposition of the saccharinato ion/ligand was given. At the same time, to the best of our knowledge, no literature data exist on the thermal behavior of the compound $[\text{Co}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$.

Another observation that led us to undertake the present study is the considerable difference in the stability of the Co and Ni compounds of the type $[\text{M}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ noticed during their preparation.⁴ Namely, although these two compounds are isomorphous, the decay of the Ni compound, probably caused by partial dehydration, is much more pronounced than that of the analogous Co complex.

In an attempt to give a correct and more precise interpretation of the thermal behavior of the isomorphous compounds $[\text{Co}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ni}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$, as well as to shed some light on the differences in their stability, their non-isothermal TG, DTG and DTA curves in a static air atmosphere, from ambient temperature up to 1000 °C were recorded at a fairly low heating rate (5 °C/min). For comparative purposes, the thermoanalytical curves of $[\text{Cu}(\text{H}_2\text{O})(\text{py})_2(\text{sac})_2]$ were also investigated. The stability and the decomposition pathways of the compounds are interpreted in relation to the structural data and their infrared spectral characteristics. A possible mode for the decomposition of the saccharinato ion/ligand is proposed. The results are compared with earlier data for the thermal decomposition of $\text{Ni}(\text{py})_2(\text{sac})_2 \cdot 8\text{H}_2\text{O}$ ⁸ and $\text{Cu}(\text{py})_2(\text{sac})_2 \cdot \text{H}_2\text{O}$.⁷

Structural data

The isomorphous Ni and Co pyridine saccharinates⁴ are triclinic, space group $P\bar{1}$. Their structures are composed of $[\text{M}(\text{H}_2\text{O})_4(\text{py})_2]^{2+}$ cations, non-coordinated saccharinato anions and non-coordinated water molecules. Each metal atom has a slightly distorted octahedral coordination. Four water molecules form the equatorial plane and two pyridine molecules are placed at the apexes. Thus, the previously supposed polymeric structure⁸ with saccharinato carbonyl and sulfonyl groups coordinated to the metal atom was found to be incorrect. All saccharinato anions and water molecules (coordinated and non-coordinated) participate in hydrogen bonding. There are *four* non-equivalent water molecules in the structure, instead of

* One of the reasons leading to this might be the appreciably high heating rate (10 °C/min)^{7,8} used in these studies

one or two as supposed previously,⁸ and only *one* type of saccharinato anions. The two pyridine molecules are structurally equivalent.

Copper pyridine saccharinate⁵ is orthorhombic, space group *Iba*2. The structure is built up of $[\text{Cu}(\text{H}_2\text{O})(\text{py})_2(\text{sac})_2]$ molecules which are hydrogen bonded to each other forming a chain structure. The copper atom is in a square pyramidal environment, the coordination polyhedron being formed by two pyridine and two saccharinato nitrogen atoms and the water oxygen atom. The two saccharinato ligands are structurally equal as are the two pyridine molecules. This eliminates the formerly supposed polymeric structure that includes metal-carbonyl and metal-sulfonyl bonds.⁷

EXPERIMENTAL

The complexes were prepared in the same way as the samples for single crystal X-ray studies.^{4,5} In order to avoid decomposition, the Co and Ni compounds were analyzed immediately after drying between folds of filter paper. Samples treated in the same way were used to check their identity by IR spectroscopy.

The DTA and TG studies were carried out on a Q derivatograph (MOM) in static air atmosphere, in the temperature range from 20 °C to approximately 1000 °C. The sample mass was 100 mg, heating rate 5 °C min⁻¹, Pt crucibles were used.

The room temperature FTIR spectra from KBr pellets or from Nujol mulls of the solid samples placed between KBr discs in the 4000 – 400 cm⁻¹ region were recorded using a System 2000 FT IR interferometer (Perkin-Elmer).

RESULTS AND DISCUSSION

Infrared data

The FT infrared spectra of the studied compounds are shown in Fig. 1. It can be noticed that, as expected, the spectra of the isomorphous Co and Ni compounds are almost identical and at the same time appreciably different from that of the Cu compound. The group of strong, broad and overlapping bands in the 3600–3000 cm⁻¹ region in the spectra of the Co and Ni compounds originate from the water stretching modes. The frequency range of the bands is in accordance with the existence of hydrogen bonds whose strength varies from weak to medium, as concluded by the structural data.⁴ A single, strong and appreciably sharp band is present in the same region of the spectrum of the Cu compound, in accordance with the existence of a single type of water with C_{2v} symmetry.^{5,10}

The saccharinato infrared bands most frequently employed for structural studies of various saccharinates are those corresponding to the stretching modes of the carbonyl and the sulfonyl groups.^{11–13} The strong bands at 1632 and 1631 cm⁻¹ for the Co and Ni compound, respectively, as well as the doublet at 1670 and 1652 cm⁻¹ for the Cu compound,¹⁰ are assigned as $\nu(\text{CO})$ modes. The existence of only one carbonyl stretching band in the spectra of the Co and Ni compounds at room temperature is in agreement with the existence of a single type of saccharinato ions.⁴ However, the appearance of two bands in the spectrum of the Cu compound, besides

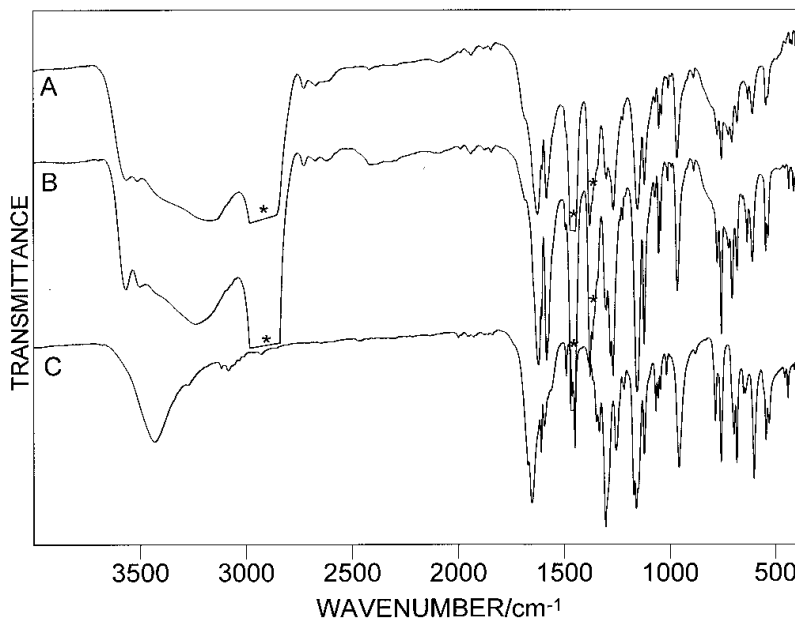


Fig. 1. FT infrared spectra of $[\text{Co}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$ (A), $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$ (B) and $[\text{Cu}(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$ (C) (asterisks denote Nujol bands).

the presence of a single type of saccharinato ions in its structure,⁵ was explained as a result of correlation splitting of the $\nu(\text{CO})$ mode.¹⁰ The lower $\nu(\text{CO})$ frequencies in the spectra of the Co and Ni compounds compared to the corresponding mode in the case of the Cu compound are in agreement with the existence of saccharinato ions^{11,12} in the structure of the former two compounds.

Usually the pair of most prominent, appreciably broad bands in the 1350–1150 cm^{-1} region for the spectra of various saccharinates are assigned to the stretching modes of the sulfonyl groups. Thus, the bands at 1266 and 1269 cm^{-1} in the spectra of the Co and the Ni compound, respectively, can be assigned to the $\nu_{\text{as}}(\text{SO}_2)$ mode, while those at 1155 (Co compound) and 1157 cm^{-1} (Ni compound) can be attributed to the $\nu_{\text{s}}(\text{SO}_2)$ mode (Fig. 1). The corresponding bands in the case of the Cu compound are found at 1303 and 1159 cm^{-1} (Fig. 1).¹⁰ The frequencies of sulfonyl stretching bands of the Cu compound are higher than the frequencies of the corresponding modes in the Co and Ni compounds, but simultaneously lower than the corresponding values for saccharin itself (1335 and 1180 cm^{-1}).¹³ The more pronounced frequency shift of the asymmetric $\nu(\text{SO}_2)$ mode is in agreement with previous conclusions that this mode is more sensitive to external influences than the symmetric $\nu(\text{SO}_2)$ mode.¹⁴ The appearance of only one pair of sulfonyl bands conforms with the existence of a single type of saccharinato ions/ligands in the structures of all studied compounds.^{4,5}

The lowering of the carbonyl and sulfonyl stretching frequencies compared to the similar modes of saccharin¹¹⁻¹³ is connected with the electron redistribution, mainly within the five-membered ring of the saccharin molecule, following its conversion to the saccharinato nitranion,¹⁵ rather than indicating coordination of saccharin to the metal atom through its carbonyl or sulfonyl groups, as previously suggested.^{7,8}

Thermal data

The relevant parts of the thermoanalytical curves of the Co, Ni and Cu compounds are shown in Figs. 2, 3 and 4, respectively. The thermal decomposition of the Co and Ni complexes will be discussed in detail, while that of the Cu complex will be mentioned only when relevant differences need to be discussed.

As can be seen by comparing Figs. 2 and 3, the thermal decomposition pathways of the Co and Ni compounds are appreciably different. The decomposition of the Co compound consists of several reasonably well resolved steps, whereas that of the Ni compound, which seems to be more complex, is composed of more overlapped steps.

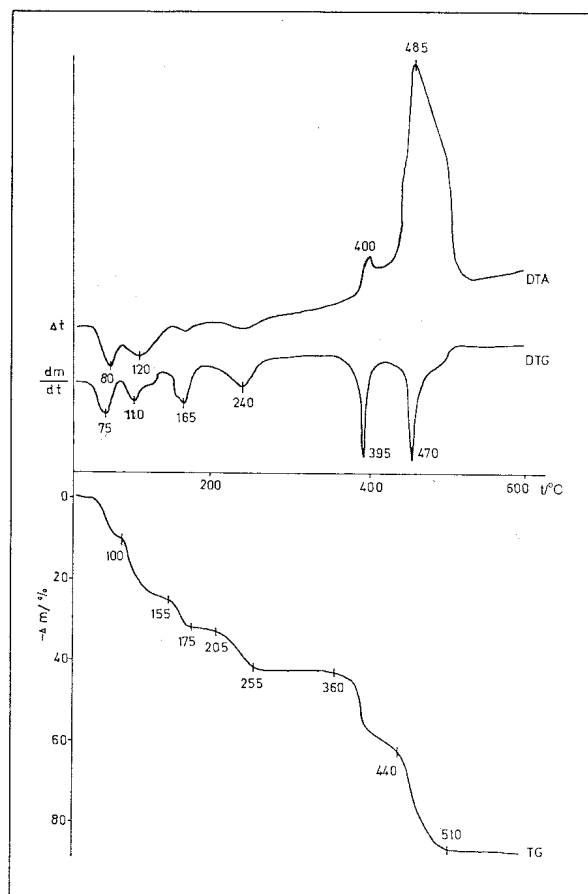


Fig. 2. Thermoanalytical curves of $[\text{Co}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$.

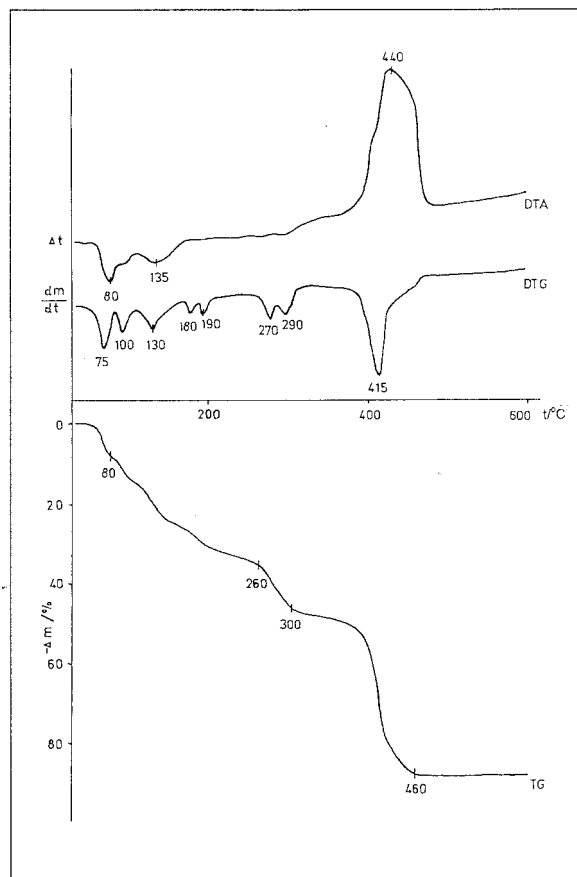
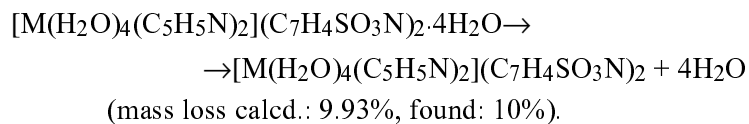


Fig. 3. Thermoanalytical curves of $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$.

Stage I: Initial dehydration of the compounds. In the first, well differentiated stage, from 70 to 100 °C for the Co complex and from 50 to 80 °C for the Ni complex, four water molecules, probably of non-coordinated water, are eliminated in a single step. The single peaks at 75 °C (DTG curves) and at 80 °C (DTA curves) correspond to this process in both cases. The higher temperature for the onset of decomposition of the Co compound compared to that of the Ni compound is in agreement with the earlier noticed higher stability of the Co compound.⁴ This is also in accordance with our finding that spectral changes in the region of the water stretching modes, as well as in the asymmetric sulfonyl stretching region, occur when the Ni complex is kept in contact with air. The structure,⁴ on the other hand, reveals hydrogen bonding between the sulfonyl groups of the saccharinato anions and the non-coordinated water molecules, consistent with the above findings.

Therefore, from this stage of the decomposition, it can be concluded that, although *two* structurally different types of *non-coordinated* water molecules exist in the structures, they leave the compounds simultaneously and can not be distin-

guished at the present heating rate. The first stage of the decomposition of the octahydrates of Co and Ni pyridine saccharinates can, therefore, be represented as follows:



The decomposition of the Cu compound (Fig. 4) starts at about 110 °C, when the crystal water is eliminated in a single step, accompanied by a single endothermic DTA peak at 145 °C. The appreciably higher dehydration temperature of the Cu compound than either the Co or the Ni compound is in agreement with the structural data⁵ and the fact that the water molecules in the Cu complex are coordinated to the metal atom.

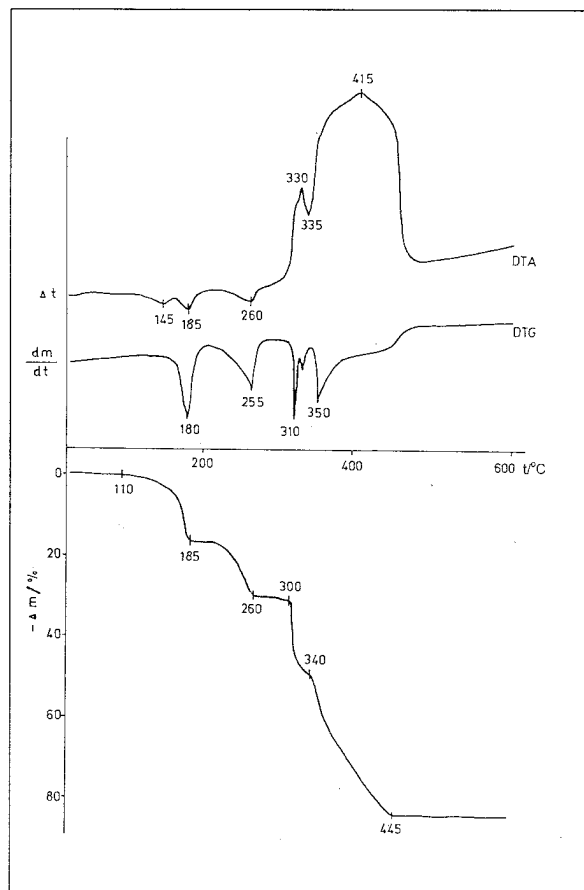
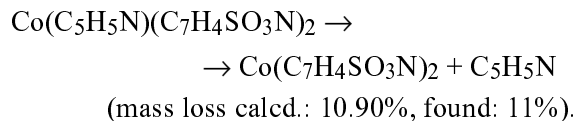
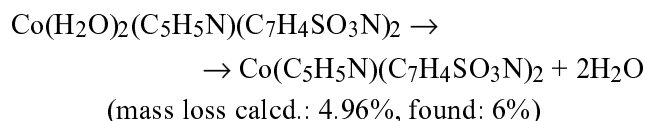
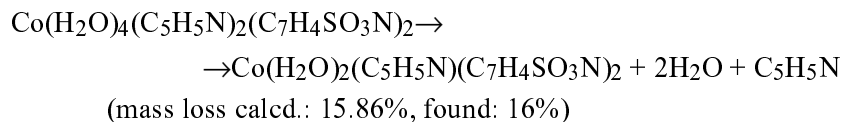


Fig. 4. Thermoanalytical curves of $[\text{Cu}(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$.

Stage II: Total dehydration and depyridination of the compounds. According to former thermal studies of $\text{Ni}(\text{py})_2(\text{sac})_2 \cdot 8\text{H}_2\text{O}$,⁸ complete two-step dehydration was believed to precede the two-step depyridination. Our studies, however, using a lower heating rate, showed that the further thermal decomposition of this complex, as well as that of the isomorphous Co compound, adopts a rather different pathway. Generally, it was found that the DTG peaks corresponding to dehydration are usually sharper, more symmetric and better defined than those connected with depyridination.

As can be seen from Figs. 2 and 3, after the first dehydration step, the decomposition of the Co and the Ni compounds adopt different pathways. Following the initial dehydration, the remaining tetrahydrate of Co pyridine saccharinate (Fig. 2) simultaneously loses two water molecules and a single pyridine molecule in the interval 100–155 °C, confirmed by the good agreement between the theoretical (15.86%) and the experimentally observed value (16%) for the mass loss (TG curve). These processes are represented by a broad, asymmetric DTG peak (110 °C) and a broad endothermic DTA peak (120 °C). The remaining two molecules of water are easily released in a single step, from 155 to 175 °C, accompanied by a DTG peak at 165 °C and a slightly endothermic effect. The second pyridine molecule is lost in the 205–255 °C interval. An excellent agreement of the calculated (10.90%) and the observed (11%) mass loss and a broad DTG peak (240 °C) correspond to the latter process. The remaining anhydrous cobalt(II) saccharinate exists in the interval from 255 up to 360 °C, as represented by the horizontal lines in the TG and DTG curves (Fig. 2).

The decomposition of the tetrahydrate of Co pyridine saccharinate up to this stage can be represented by the following equations:

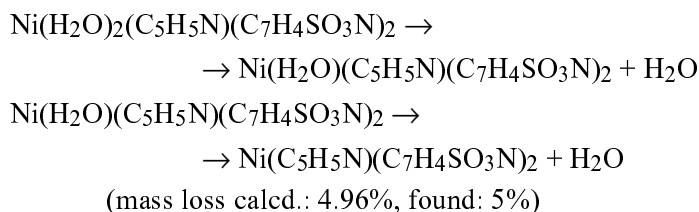
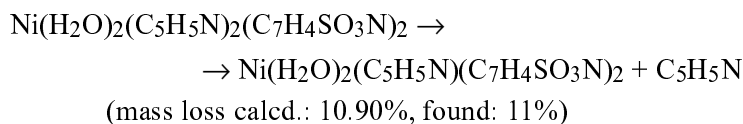
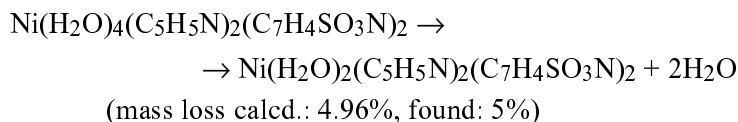


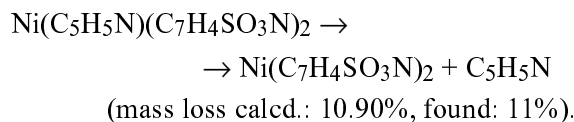
The dehydration of the tetrahydrate of the Co compound in two distinct processes is in agreement with the fact that the *four coordinated* molecules are of *two* types,⁴ differing in the strength of the bond to the metal atom. It is obvious,

however, that as soon as this structure is thermally damaged, the metal–pyridine bonds become weaker and one of the pyridine molecules is easily released together with the water. On further heating, the two more strongly bonded water molecules leave the molecule in a single step, followed by complete depyridination. It is obvious from the DTA curve (Fig. 2), that once the structure of the tetrahydrate is disturbed, the remaining residue is fairly labile, so that the further dehydration and depyridination proceed accompanied by very weak endothermic effects.

After the release of the initial four water molecules, the decomposition of Ni pyridine saccharinate proceeds in several overlapping endothermic steps (Fig. 3). However, on the basis of the inflection points on the TG curve, approximate estimations of the corresponding temperature intervals could be made. In the first step, from about 90 °C to 110 °C, only two of the four water molecules are eliminated (DTG peak at 100 °C, calculated and observed mass losses of 4.96% and 5%, respectively). Subsequently, a pyridine molecule is released (calculated mass loss 10.90%, found 11%), accompanied by a single and relatively broad DTG peak at 130 °C and an endothermic effect (DTA peak at 135 °C). The two remaining water molecules are lost continuously. The two very close DTG peaks at 180 and 190 °C correspond to these processes. In the 260–300 °C temperature interval, the other pyridine molecule leaves the residue. A doublet of DTG peaks (270 and 290 °C) are present in this interval. However, no explanation for the appearance of two peaks corresponding to this process can be given at this moment. In the case of the Ni compound, contrary to the Co complex, no temperature interval was observed where the anhydrous depyridinated saccharinate exists.

The decomposition of the tetrahydrate of Ni pyridine saccharinate up to this stage can be described by the following equations:





As in the case of the Co compound, the dehydration of Ni pyridine saccharinate tetrahydrate proceeds in *two* separate steps, due to the existence of *two* types of water coordinated to the metal atom.⁴ The primary depyridination of the Ni compound (130 °C) occurs at a higher temperature compared to the Co compound (110 °C) indicating that, even at this stage of decomposition, the metal–pyridine bonds in the Ni are somewhat stronger than the corresponding bonds in the Co compound, analogous to information revealed by the structural data of the initial compounds.⁴ Namely, the metal–pyridine bonds in $[\text{Ni}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ are shorter (2.130 Å) than in $[\text{Co}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ (2.186 Å).⁴

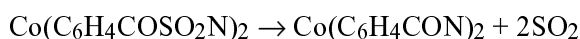
After the rearrangement of the structure, however, the two remaining water molecules are in slightly different environments, so they leave the residue in two consecutive but very close steps. The temperatures corresponding to the DTG peaks of both steps (180 and 190 °C), are higher than the temperature of the corresponding process for the Co compound (165 °C).

The depyridination of the Cu compound (Fig. 4) is similar to the one reported previously for a compound with the same stoichiometry.⁶ After dehydration, the two pyridine molecules coordinated to the metal become non-equivalent and are lost in two consecutive steps (DTG peaks at 180 and 255 °C with DTA peaks at 185 and 260 °C, respectively). The anhydrous and depyridinated compound is stable between 260 and 300 °C. The temperature for the initial depyridination of the Cu complex (180 °C) is appreciably higher than the corresponding temperatures for the Co (110 °C) and the Ni compound (130 °C), indicating stronger metal–pyridine bonding in the first compound.

Stage III: Decomposition of the metal(II) saccharinates. From some earlier thermal studies,¹⁶ it is known that the decomposition temperature of pure saccharin is lower than that of the saccharinato ligand. On the other hand, the decomposition temperature of the saccharinato ligand is lower in the pyridine adducts of the saccharinates compared to the corresponding metal(II) saccharinates.^{7,8} Without any firm basis, a two-step mechanism for the decomposition of the saccharinato ligand in an oxidizing atmosphere was suggested recently.¹⁶ According to this mechanism, oxidation of the benzene ring was supposed in the first step. Having in mind the large exothermic effect expected for this process, the supposed mechanism seemed rather doubtful to us.

In the case of the Co compound (Fig. 2), the saccharinate decomposition occurs in two consecutive steps. The first part of the decomposition proceeds in the 360 – 440 °C interval and is accompanied by a weak exothermic peak at 400 °C and a DTG peak at 395 °C. A large asymmetric exothermic peak, with a maximum at

485 °C, as well as a DTG peak at 470 °C correspond to the second step (440–510 °C). Since it is difficult to give an exact explanation of the processes involved in the combustion of an organic residue containing, in addition to carbon, nitrogen and sulfur, in an oxidizing atmosphere, it is only possible to envisage the overall decomposition processes. Considering the coordination through the saccharinato nitrogen atom, on the one hand, and the stability of the six-membered benzene ring on the other, as well as on the basis of the TG and DTG curves, it seems reasonable to suppose that in the first step dissociation of the sulfonyl group to sulfur dioxide takes place. Subsequently, the remaining organic residue is oxidized. One of the possible ways to express the decomposition of the saccharinato residue, therefore, would be as it follows:



(mass loss calcd.: 17.66% found: 17.5%)



(mass loss calcd. on Co_2O_3 : 32.80%, found: 33%).

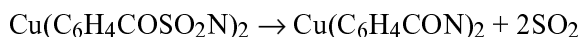
The decomposition of the Ni saccharinate (Fig. 3) seems different to that of the Co compound. Namely, in the case of the Ni compound, as it follows from a comparison of the theoretical and the experimental values of the mass loss, the two oxidation steps of the saccharinato groups are not resolved. One large and asymmetric exothermic DTA peak (440 °C), as well as an asymmetric DTG peak (415 °C), are connected with the oxidation. The decomposition continues up to 460 °C. Contrary to previous observations,⁸ no effects of mass-gain of the residue were noticed, probably due to the lower heating rate. In fact, a slight decrease in the mass residue was observed (not shown in Fig. 3) which can be explained as being due to a stabilization of the structure of the resulting NiO. The decomposition of the saccharinato residue in this case could be represented as:



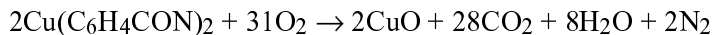
(mass loss calcd. on NiO: 45.80%, found: 46%).

Although the decomposition of the Cu compound was investigated previously,⁶ no explanation for the decomposition of the saccharinato ligand was given.

The two-step decomposition (Fig. 4) is accompanied by two exothermic DTA peaks at 330 and 415 °C, as well as by two corresponding DTG peaks at 310 and 350 °C. As it can be noticed by the reactions given below, there is in excellent agreement between the calculated and the observed mass loss values, which supports the supposed decomposition mechanism:



(mass loss calcd.: 21.20%, found: 21%)



(mass loss calcd. on CuO: 33.80%, found: 34%).

Acknowledgement: The financial support of the Ministry of Science of the Republic of Macedonia is gratefully acknowledged.

ИЗВОД

ТЕРМИЧКО РАЗЛАГАЊЕ Co, Ni И Cu ПИРИДИН САХАРИНАТА: КОРЕЛАЦИЈЕ СА СТРУКТУРНИМ И ИНФРАЦРВЕНИМ ПОДАЦИМА

ПАНЧЕ НАУМОВ,¹ ГЛИГОР ЈОВАНОВСКИ,¹ ВЕРА ЈОРДАНОВСКА¹ И БОЈАН БОЈАНОВ²

¹Институт за хемију, Природно-математички факултет, Универзитет "Св. Кирил и Методиј", бр. 162,
91001 Скопје, Македонија и

²Хемијски факултет, Универзитет у Пловдиву, Паиси Хилендарски, 4025, Пловдив, Бугарска

У циљу проучавања разлика у стабилности изоморфних пиридин сахарината $[\text{Co}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$ и $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot 4\text{H}_2\text{O}$, испитивано је њихово термичко понашање (TG, DTG и DTA криве) у статичној ваздушној атмосфери у интервалу од собне температуре до 1000 °C. Ради компарације снимљене су и термоаналитичке криве бакарног комплекса $[\text{Cu}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_5\text{N})_2](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2$. Начин термичког разлагања и стабилност једињења интерпретовани су подацима о њиховим кристалним структурама. Предложен је механизам разлагања сахаринатног јона/лиганда у оксидационој атмосфери. Дискутоване су и карактеристике инфрацрвених спектра проучаваних комплекса.

(Примљено 16. фебруара 1999)

REFERENCES

1. N. Suzuki, H. Suzuki, *Cancer Res.* **55** (1995) 4253
2. F. A. Cotton, L. R. Falvello, R. Llusar, E. Libby, C. Murillo, *Inorg. Chem.* **25** (1986) 3423
3. O. V. Quanzani, S. Tarulli, O. E. Piro, E. J. Baran, E. E. Castellano, *Z. Naturforsch.* **52b**(1996) 183
4. G. Jovanovski, P. Naumov, O. Grupče, B. Kaitner, *Eur. J. Solid State Inorg. Chem.* **35** (1998) 579
5. G. Jovanovski, P. Naumov, O. Grupče, B. Kaitner, *Eur. J. Solid State Inorg. Chem.* **35** (1998) 231
6. O. Grupče, G. Jovanovski, B. Kaitner, P. Naumov, *Croat. Chem. Acta*, in press
7. A. D. Magri, G. D'Ascenzo, S. Nunziantes Cesaro, E. Chiacchierini, *Thermochim. Acta* **36** (1980) 279
8. G. D'Ascenzo, R. Curini, A. Marino, A. Magri, E. Chiacchierini, *Thermochim. Acta* **59** (1982) 63
9. U. K. R. Romman, K. M. A. Malik, S. Z. Haider, *J. Bangladesh Acad. Sci.* **17** (1993) 165
10. P. Naumov, G. Jovanovski, O. Grupče, *J. Mol. Struct.*, **482-483** (1999) 121
11. G. Jovanovski, B. Šoptrajanov, *J. Mol. Struct.* **174** (1988) 467
12. G. Jovanovski, B. Šoptrajanov, B. Kamenar, *Bull. Chem. Technol. Macedonia* **8** (1990) 47
13. G. Jovanovski, S. Tančeva, B. Šoptrajanov, *Spectrosc. Lett.* **28** (1995) 1095
14. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 360
15. I. G. Binev, B. A. Stamboliyska, E. A. Velcheva, *Spectrochim. Acta* **52A** (1996) 1135
16. Z. Yugeng, *Transit. Met. Chem.* **19** (1994) 446.