

COORDINATION COMPOUNDS OF BIOLOGICAL INTEREST: THERMAL PROPERTIES OF SOME COMPOUNDS OF SACCHARIN (*o*-BENZOIC SULPHIMIDE) WITH NICKEL(II) AND ZINC(II)

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ABSTRACT

The thermal properties of nickel(II) and zinc(II) complexes of saccharin (sacc) (*o*-benzoic sulphimide) have been studied and compared both with those of cobalt(II) and copper(II) previously studied and with those of ternary complexes of nickel(II) and zinc(II) having both saccharin and pyridine as ligands. The thermal behaviour is discussed in terms of the interaction between metal and ligands, interaction studied by IR spectroscopy, and by reflectance spectroscopy.

The classical thermal stability scale $\text{Co(II)} > \text{Ni(II)} > \text{Cu(II)} < \text{Zn(II)}$ is always obtained.

INTRODUCTION

Following the study of complexes between ligands of pharmaceutical importance and trace elements existing in the body fluids, we studied by thermal and spectroscopic techniques the coordination compounds of saccharin (sacc) (*o*-benzoic sulphimide) with nickel(II) $[\text{Ni}(\text{sacc})_2] \cdot 6 \text{H}_2\text{O}$ and zinc(II) $[\text{Zn}(\text{sacc})_2] \cdot 6 \text{H}_2\text{O}$. The study was undertaken both as a continuation of the systematic investigation in this field [1] carried out by the School of Analytical Chemistry and because of the increasing importance of zinc and its coordination compounds in human physiology and pathology with particular reference to arterial hypertension, where the role of the zinc(II) becomes more and more important because its interaction with angiotensin-converting enzyme [2] and also drugs such as saccharin that can give coordination compounds with zinc(II) which can modify its biological activity.

The properties of the cited compounds have been compared with those of

ternary complexes obtained by reaction of saccharin and pyridine (pyr) with the same metal ions to give $[\text{Ni}(\text{sacc}_2\text{pyr}_2)] \cdot 8 \text{H}_2\text{O}$ and $[\text{Zn}(\text{sacc}_2\text{pyr}_2)] \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

Instrumentation

The TG, DTG and DTA curves were obtained using a DuPont Model 990 DTA cell and console, and a Model 951 Thermobalance. The heating rate used was $10^\circ\text{C min}^{-1}$ on samples whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of either dry nitrogen or air, at a flow rate of 50–100 ml min^{-1} . All temperatures were corrected for thermocouple non-linearity and are, of course, procedural decomposition temperatures (pdts).

The TG and DTA analyses were carried out using a quartz sample holder because platinum crucibles would interact with the saccharin sulphur. Aluminum oxide crucibles were used for the DTA analysis.

The IR spectra were recorded using a Beckman IR 12 instrument. The reflectance spectra were recorded using a Beckman Model DK-2A spectrophotometer equipped with a heated sample holder as previously described [3].

Preparation of compounds

Saccharin (EGA-Chemie K.G., Germany) was used. The other chemicals employed were all of reagent-grade quality. All the compounds were prepared according to the methods proposed by Zwickler [4] and Biedermann [5], and were checked by elemental analysis. The results obtained are in good agreement with those calculated for the proposed formulae.

RESULTS

The decomposition trend is typical for each one of the two series and similar to those of the cobalt(II) and copper(II) complexes studied earlier [1]. The binary saccharin coordination compounds lose the water of hydration in a single step (Figs. 1 and 2). The anhydrous compounds obtained decompose in two steps, resolved in the case of the zinc compound and superimposed for the nickel compound, to give a mixture of sulphate and sulphide. The latter is then oxidized in air, but not in nitrogen, to give sulphate, as shown by the mass gain starting after the decomposition of the ligand. The sulphate then dissociates to the oxide.

The DTA curves (Figs. 1 and 2), both in air or in nitrogen, show only one endothermic peak for the loss of water. The decomposition occurs in air

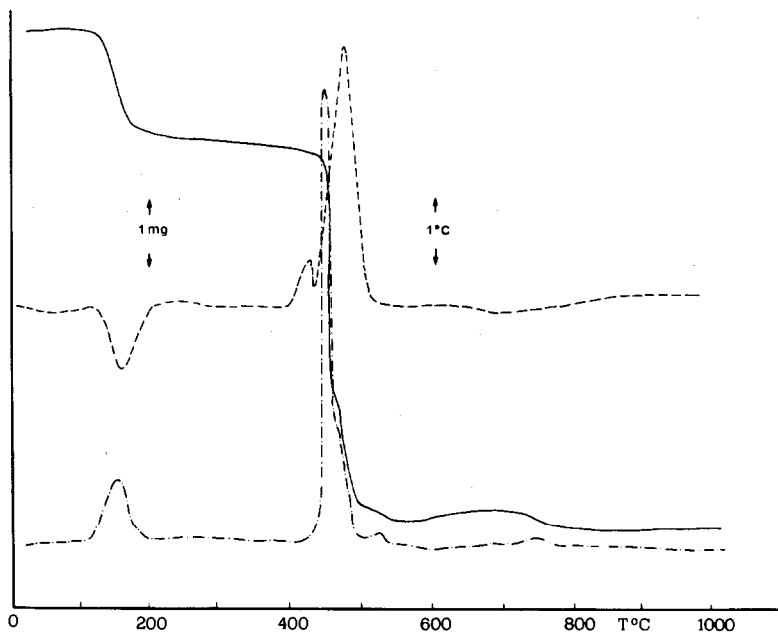


Fig. 1. TG (—), DTG (— · — · —), and DTA (---) curves of $[\text{NiSacc}_2] \cdot 6 \text{H}_2\text{O}$ in an atmosphere of air. Heating rate $10^\circ\text{C min}^{-1}$.

through two superimposed exothermic peaks, the first one small for the zinc and scarcely evident for the nickel, while the second is large and sharp. In nitrogen, two endothermic peaks represent the decomposition.

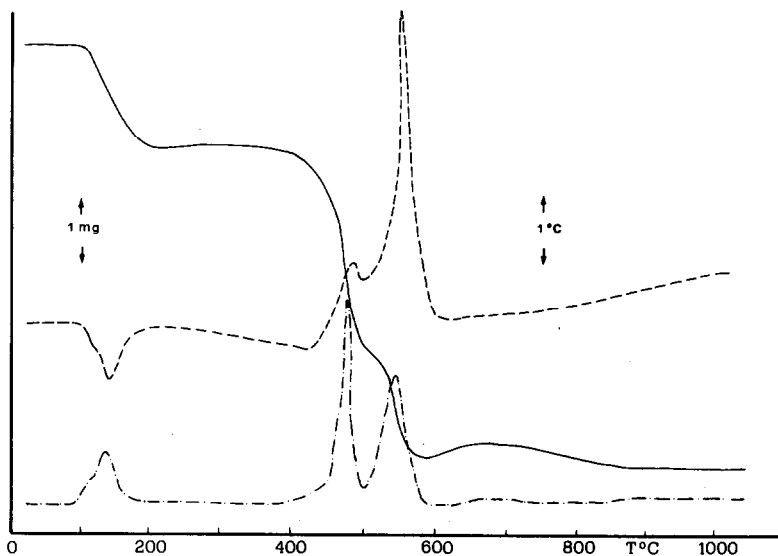


Fig. 2. TG (—), DTG (— · — · —), and DTA (---) curves of $[\text{ZnSacc}_2] \cdot 6 \text{H}_2\text{O}$ in an atmosphere of air. Heating rate $10^\circ\text{C min}^{-1}$.

The ternary complexes show that the dehydration process takes place in two completely superimposed steps for the nickel compound (Fig. 3), which correspond on the DTA curve to two unresolved endothermic peaks, while for the zinc compound (Fig. 4), only one molecule of water is lost in one endothermic process. The dehydration process is followed by the loss of the two pyridine molecules for both compounds, but the nickel compound loses the two pyridine molecules in two indistinct steps, while the same process occurs for the zinc compound at two well-defined temperatures. The decomposition behaviour of the residue shows the same shape as that of the anhydrous compounds of the previous series, but occurs at a slightly lower temperature.

For the nickel compound (Fig. 3), the DTA curves show two superimposed endothermic peaks, both in nitrogen and in air, corresponding to the release of the two pyridine molecules, while the same process for the zinc compound (Fig. 4) is represented by two well-separated endothermic peaks. The decomposition trends of the residue give a plot identical to that of the anhydrous compounds of the earlier series, but at a slightly lower temperature.

The anhydrous saccharin compound and the residue of the ternary complexes after the release of the pyridine molecules seem to be identical as confirmed by the high temperature reflectance spectra and by the dynamic reflectance spectra [6], which are identical for both the species.

The decomposition temperatures are summarized in Table 1. Figures 1

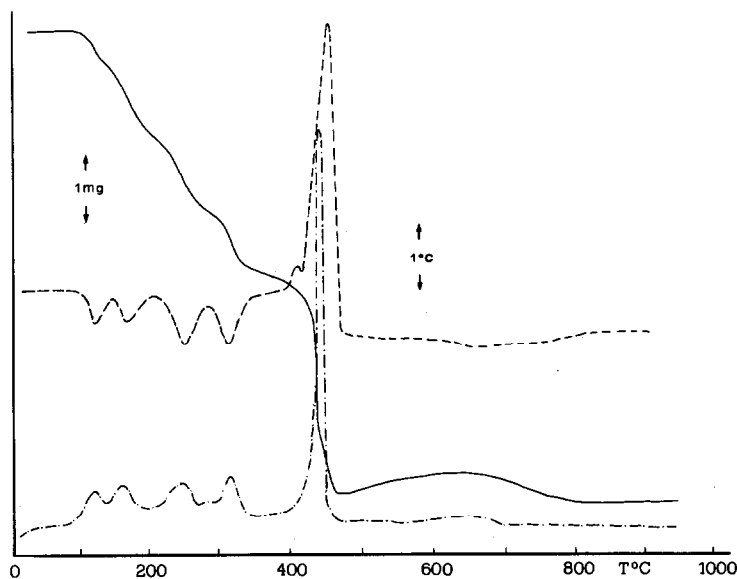


Fig. 3. TG (—), DTG (---), and DTA (- - -) curves of $[\text{Nisacc}_2\text{pyr}_2] \cdot 8 \text{H}_2\text{O}$ in an atmosphere of air. Heating rate $10^\circ\text{C min}^{-1}$.

TABLE I

Procedural decomposition temperatures from TG and DTA curves (air atmosphere) Processes following the decomposition of the ligand are omitted.

Compound	TG			DTA				
	H ₂ O	Step I	Step II	Step III	H ₂ O	Peak I	Peak II	Peak III
[Zn(sacc) ₂]·6 H ₂ O	140 ^a 100–195 ^b	470 400–500	545 500–570		135 ^c 105–190	470 420–495	535 495–570	
[Zn(sacc) ₂ pyr ₂]·H ₂ O	140 130–150	200–240 170–315	455 375–480	540	140 125–150	200–240 180–315	450 380–470	550 490–570
[Ni(sacc) ₂]·6 H ₂ O	155 120–200	450 395–520			150 120–195	450–470 395–510		
[Ni(sacc) ₂ pyr ₂]·8 H ₂ O	120–165 95–210	250–315 210–340	435 350–470		115–160 95–205	245–310 205–340	435–450 350–465	

^a Maximum rate.

^b Temperature at beginning and end of reaction.

^c Peak minimum or maximum.

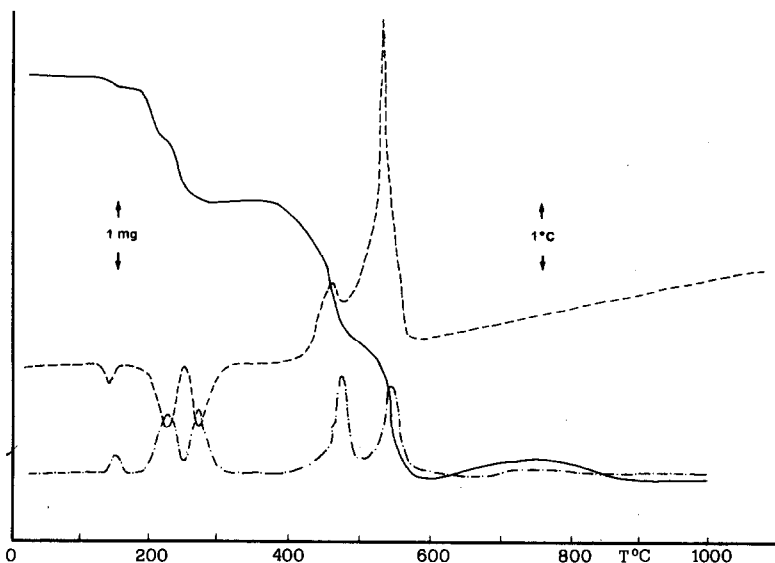


Fig. 4. TG (—), DTG (---), and DTA (- - -) curves of $[\text{Znsacc}_2\text{pyr}_2] \cdot \text{H}_2\text{O}$ in an atmosphere of air. Heating rate $10^\circ\text{C min}^{-1}$.

and 2 show the TG, DTG and DTA curves for the nickel compounds, while Figs. 3 and 4 show the TG, DTG and DTA curves for the zinc compounds.

DISCUSSION

Looking at the initial decomposition temperatures of the anhydrous compounds of the series $(\text{Msacc}_2) \cdot n\text{H}_2\text{O}$ where $\text{M} = \text{cobalt(II)}$ [1], copper(II) [1], nickel(II) and zinc(II) , it is possible to find a classical trend [7] of the thermal stability: $\text{Co(II)} > \text{Ni(II)} > \text{Cu(II)} < \text{Zn(II)}$.

The series of ternary compounds shows the same behaviour. It is interesting to note that the decomposition temperatures of the anhydrous compounds of the saccharin series are slightly higher than those corresponding to the same compounds obtained after the loss of the two pyridine molecules present in the ternary complexes.

This phenomenon can be explained when it is considered that the crystal structure after the release of the two pyridines is not so organized as in the anhydrous saccharin compound, so the decomposition is easier and starts first.

IR spectra analysis can elucidate the nature of the bonds between the central ion and the ligands and supports the thermal decomposition behaviour of the two series. The carbonyl and sulphonyl group frequencies (Table 2) are lower, for both series of compounds, than those corresponding to the saccharin alone, indicating the presence of a metal–ligand bond,

TABLE 2
Frequencies (cm^{-1}) of carbonyl and sulphonyl groups

Assignment	Saccharin	[Nisacc ₂] · 8 H ₂ O	[Nisacc ₂ pyr ₂] · 6 H ₂ O	[Zasacc ₂] · 6 H ₂ O	[Zasacc ₂ pyr ₂] · H ₂ O
C-O	1675	1606	1636	1619	1642
ν_1 SO ₂ (symmetric stretching)	1160	1135	1156	1131	1155
ν_3 SO ₂ (asymmetric stretching)	1312	1270	1290	1251	1283

which accounts also for the formation of sulphate and sulphite during the decomposition. At the same time, the frequencies of the carbonyl and sulphonyl groups are higher for the ternary complexes than for the binary complexes, indicating that the presence of pyridine in the coordination sphere weakens the saccharin-metal bonds. The N-H bond in the pure saccharin interacts with the SO_2 giving an absorption at about 2970 cm^{-1} [8], which disappears in the complexes. The N-H stretching, weak and flat, falls in a spectral region where O-H and O-H (water) stretching absorption are prominent and also, working on the dehydrated compounds, it is impossible to locate the N-H stretching. At the same time, the presence of an N-H bending frequency and of a ring vibration make impossible the use of the N-H maximum at 1490 cm^{-1} .

Finally, the water of hydration of the compounds is, in practice, of only one type. At the same time, the reflectance spectra show an octahedral structure for cobalt(II) [1] and nickel(II) and a distorted octahedral structure for copper(II) [1] compounds. In these structures, it is probable that four positions are bound to the carbonyl group of two saccharin molecules and to the sulphonyl group of two other saccharin molecules, while the remaining sulphonyl and carbonyl groups of each molecule interact with other metal ions giving a polymeric structure with a molar metal:saccharin ratio of 1:2. The remaining two octahedral positions not bound to the water, which would be of two types if present in the coordination sphere, interact with the pyridinic nitrogen in the case of the ternary complexes and with the N-H group of the saccharin in the absence of pyridine, giving a chelate structure that stabilizes these compounds.

This possible structure agrees with the higher frequencies obtained in the IR spectra for carbonyl and sulphonyl groups of the ternary complexes compared with those of the binary complexes and allows the higher thermal stability of the anhydrous saccharin compounds to be justified with respect to the same species obtained from the ternary complexes after the loss of the pyridine molecules.

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