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COORDINATION COMPOUNDS OF BIOLOGICAL INTEREST: THERMAL PROPERTIES OF SOME COMPOUNDS OF SACCHARIN (*o*-BENZOIC SULFIMIDE) WITH DIVALENT METAL IONS

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ABSTRACT

The thermal properties of cobalt(II) and copper(II) complexes of saccharin (sacc) (*o*-benzoic sulfimide) have been studied, and are compared with those of ternary complexes of cobalt(II) and copper(II) having both saccharin and pyridine as ligands. The thermal behaviour is discussed in terms of the bonds between the central ion and the ligands. The frequency shifts of the carbonyl and sulfonyl groups support the hypotheses derived from the thermal data. The thermal stability scale Co(II) > Cu(II) is always obtained while the stability constant scale is Co(II) < Cu(II).

INTRODUCTION

Because of the interest shown in complexes between ligands of pharmaceutical importance and trace elements existing in the body fluids, we have undertaken a systematic investigation, by thermal and spectroscopic techniques, of some compounds of saccharin (sacc) (*o*-benzoic sulfimide) with divalent metal ions such as cobalt(II), nickel(II), copper(II) and zinc(II). The cobalt(II) and copper(II) complexes $[Cosacc_2] \cdot 6\ H_2O$ and $[Cusacc_2] \cdot 5\ H_2O$ were studied first because of their higher concentration and biological activity. Data concerning these compounds are reported here, while the investigation of nickel(II) and zinc(II) complexes is still in progress.

The properties of the compounds studied have been compared with those of ternary complexes of saccharin and pyridine (pyr) having the same central ion, including $[Cosacc_2pyr_2] \cdot H_2O$, $[Cosacc_2pyr_2] \cdot 4\ H_2O$, $[Cusacc_2pyr_2] \cdot H_2O$, $[Cusacc_2pyr_2] \cdot 2\ H_2O$, and $[Cusacc_2pyr_2] \cdot 4\ H_2O$.

EXPERIMENTAL

Instrumentation

The TG, DTG and DTA curves were obtained using a Du Pont Model 990 DTA cell and console, and a Model 951 thermobalance. The heating rate used was 10°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 (pdt's). 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 spectro-reflectometer equipped with a heated sample holder as previously described [1].

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 Zwikker [2] and Biedermann [3], and were checked by elemental analysis. The results obtained are in good agreement with those calculated for the proposed formulae.

RESULTS

It is possible to observe a typical decomposition trend for each of the two series. The saccharin complexes lose the water of hydration in a single step. The anhydrous compounds so obtained decompose to give a mixture of the sulfate and the sulfide; the latter is then oxidized in an atmosphere of air, but not in one of nitrogen, to give the sulfate, which accounts for the mass gain starting after the decomposition of the ligand. The sulphate then dissociates to the oxide.

The DTA curves for samples in atmospheres of nitrogen and of air show only one endothermic peak, corresponding to total loss of water. When an atmosphere of air is used, the decomposition is indicated by two superimposed exothermic peaks, the first very small, and the second large and sharp. When a nitrogen atmosphere is used, the decomposition is indicated by two endothermic peaks.

The thermal curves of the ternary complexes show that after the first single step, corresponding to the total dehydration, there is double step, corresponding to the loss of two pyridine molecules.

The decomposition trend of the residue is similar to that of the anhydrous compounds of the previous series, but occurs at a slightly lower temperature.

TABLE 1

Procedural decomposition temperatures from TG and DTA curves (air atmosphere) (processes following decomposition of ligands are omitted)

Compound	TG				DTA			
	H_2O	Step I	Step II	Step III	H_2O	Peak I	Peak II	Peak III
$\mathrm{Cosacc_2 \cdot 6\,H_2O}$	130 [a] 90–150 [b]	420 410–450	530 500–560		125 [c] 100–140	425 405–440	525 490–550	
$\mathrm{Cosacc_2pyr_2 \cdot H_2O}$	115 90–135	260 245–280	410 370–440	520 480–540	110 100–130	255 245–275	410 380–430	520 480–540
$\mathrm{Cosacc_2pyr_2 \cdot 4\,H_2O}$	115 80–140	260 245–280	410 375–445	525 480–535	115 90–135	260 245–275	410 380–435	520 480–535
$\mathrm{Cusacc_2 \cdot 5\,H_2O}$	110 70–170	300 270–310	360 310–400		110 80–140	300 290–310	330–370 310–400	
$\mathrm{Cusacc_2pyr_2 \cdot H_2O}$	150 130–165	195 165–205	250 230–270	340–355 305–360	150 140–170	195 170–210	265 240–280	340–380 310–400
$\mathrm{Cusacc_2pyr_2 \cdot 2\,H_2O}$	150 125–165	200 165–210	250 235–275	340–355 305–360	150 135–170	200 170–210	265 240–280	335–375 305–395
$\mathrm{Cusacc_2pyr_2 \cdot 4\,H_2O}$	150 120–165	195 165–210	250 230–250	340–355 305–360	150 130–170	200 170–210	260 235–270	335–375 305–395

[a] Maximum rate.

[b] Temperatures at beginning and end of reaction.

[c] Peak minimum.

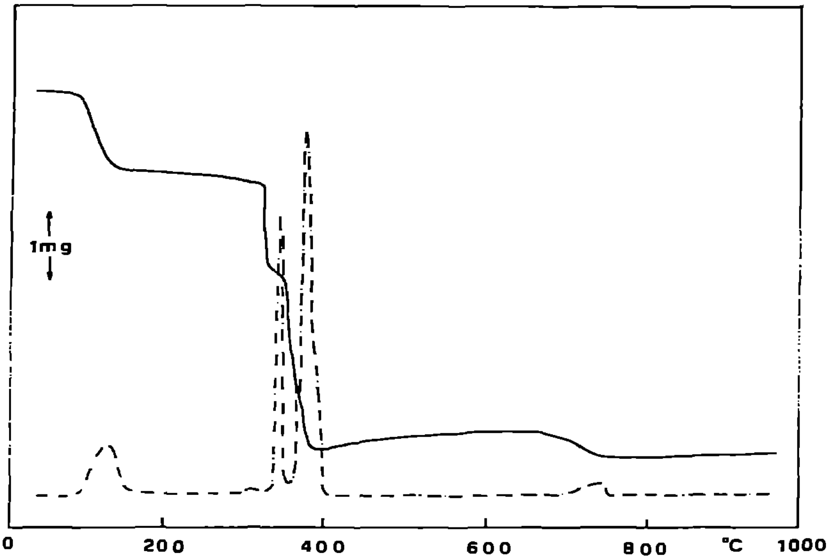

Fig. 1. TG and DTG curves of $Cusacc_2 \cdot 5\ H_2O$. (———) TG and (— · — ·) DTG curves in an atmosphere of air. Heating rate 10°C min^{-1}.

When atmospheres of either nitrogen or air are used, the DTA curves show only one endothermic peak for the dehydration and two endothermic peaks, each one corresponding to the release of one pyridine molecule. The area of each single-pyridine peak is bigger than that of the peak corresponding to total dehydration, indicating that the pyridine is more strongly bound than the water, which is the last one not to be included in the coordination sphere.

The decomposition then occurs, giving a plot identical to that of the

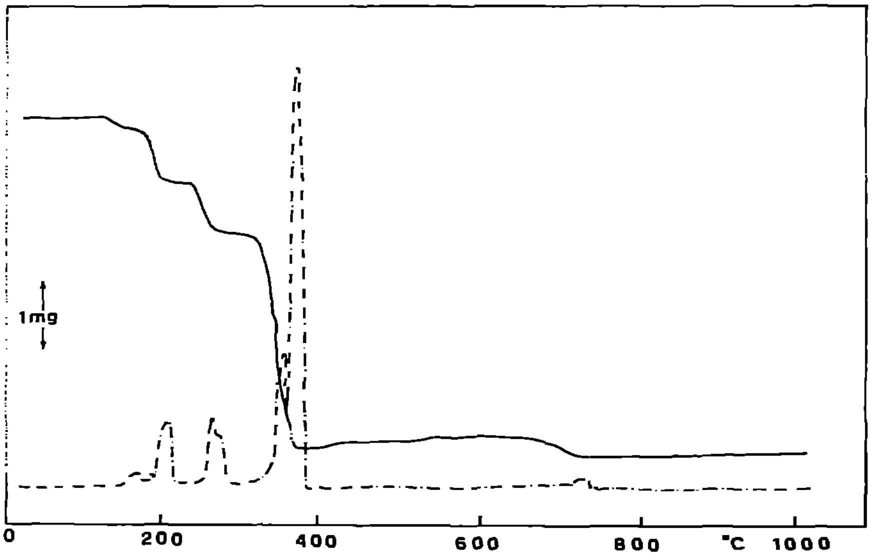

Fig. 2. TG and DTG curves of $Cusacc_2pyr_2 \cdot H_2O$. (———) TG and (— · — ·) DTG curves in an atmosphere of air. Heating rate 10°C min^{-1}.

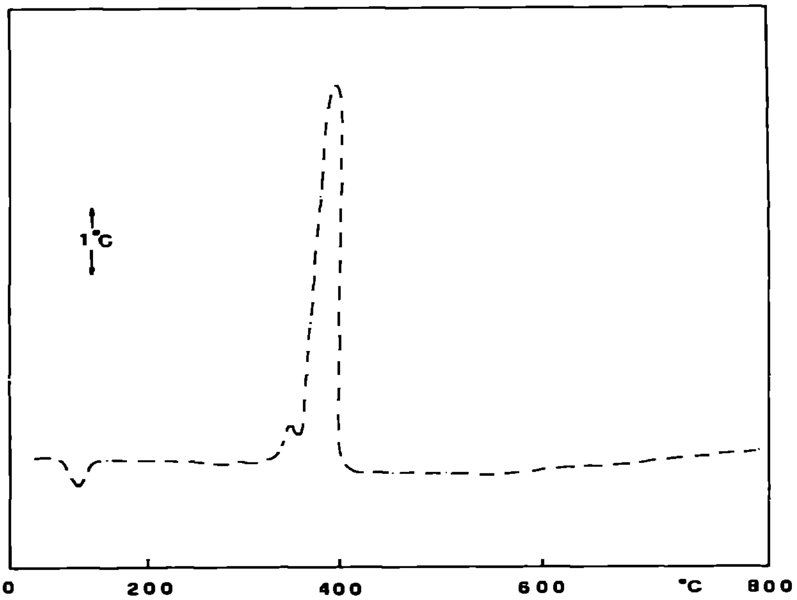

Fig. 3. DTA curve of Cusacc$_2$ · 5 H_2O in an atmosphere of air. Heating rate 10°C min^{-1}.

anhydrous compounds of the upper series, but at a slightly lower temperature.

The anhydrous saccharin compound and the compound obtained from the ternary complexes after the loss of the pyridine molecules seem to be the same as shown by the high-temperature reflectance spectra. In fact, the spectrum of the anhydrous pyridine compound and that of the compound

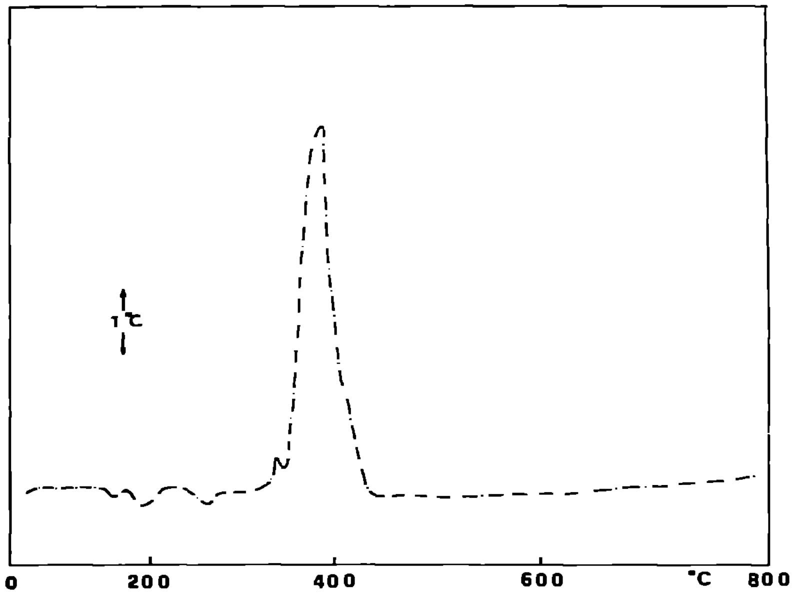

Fig. 4. DTA curve of Cusacc$_2$pyr$_2$ · H_2O in an atmosphere of air. Heating rate 10°C min^{-1}.

obtained from the ternary complex at the end of the pyridine loss are exactly the same. The slightly lower thermal stability of the latter can be explained if we consider that the decomposition begins after the loss of the two pyridine molecules: the crystal structure is probably not as organised as in the anhydrous pyridine compound, so that decomposition is easier and starts first.

The decomposition temperatures are summarized in Table 1. Figures 1 and 2 show, as an example, the TG and DTG curves of [$Cusacc_2$] · 5 H_2O and of [$Cusacc_2pyr_2$] · H_2O, while Figs. 3 and 4 show the DTA curves of the same compounds; all of these curves were recorded for samples in an atmosphere of air.

DISCUSSION

From the thermal data it is possible to see that: (a) the water is always lost in a single process; (b) the pyridine is always lost in two steps, which occur before the decomposition; (c) the decomposition gives the sulphide and the sulphate; (d) the decomposition temperature of the anhydrous compound, M(II)$sacc_2$, obtained from the complexes containing saccharin alone is higher than that corresponding to the anhydrous compound obtained from the mixed complexes after dehydration and release of the two pyridine molecules. This behavior can be explained by considering the nature of the bonds between the central ion and the ligands.

Looking at the IR spectra it is possible to see that the carbonyl and sulfonyl group frequencies (Table 2) are lower for these compounds than those for saccharin (whose frequencies are in very good agreement with those referred to by O'Sullivan [4]), indicating the presence of a metal—ligand bond, in accordance with the formation of the sulphide and the sulphate during the decomposition.

The N—H bond in the pure saccharin interacts with the SO_2, giving an absorption at about 2970 cm^{-1} [4]. This absorption disappears in the complexes. It is practically impossible to locate the N—H stretching because it is weak and flat, and falls in a spectral region where O—H and O—H (water) stretching absorptions are prominent. Further, heating the compound to total dehydration produces no appreciable change. It is also impossible to bypass the problem by using the N—H maximum near 1490 cm^{-1} because an N—H bending frequency and a ring vibration are also sometimes present in this region.

It is interesting to note that the presence of the pyridine in the coordination sphere weakens the metal—ligand bonds between the sulfonyl, and especially the carbonyl groups, and the central ion, as shown by the fact that the corresponding frequencies are lower with respect to those of saccharin, but higher with respect to those of the metal—saccharin complexes.

Looking now at the hydration water of all the compounds, it is possible to see that in every case the last water molecule is lost in a single step, indicating that there is only one type of water molecule present. At the same time, the reflectance spectra show an octahedral structure for the cobalt(II)

TABLE 2

Frequencies (cm^{-1}) of carbonyl and sulfonyl groups

Assignment	Saccharin	Cosacc$_2$ · 6 H_2O	Cosacc$_2$ pyr$_2$ · H_2O	Cosacc$_2$ pyr$_2$ · 4 H_2O	Cusacc$_2$ · 5 H_2O	Cusacc$_2$pyr$_2$ · H_2O	Cusacc$_2$ pyr$_2$ · 2 H_2O	Cusacc$_2$ pyr$_2$ · 4 H_2O
C—O	1675	1564	1618	1618	1617	1646	1646	1646
ν_1 SO_2 (symmetric stretching)	1160	1126	1157	1158	1163	1158	1156	1158
ν_3 SO_2 (assymmetric stretching)	1312	1262	1282	1286	1304	1301	1303	1301

compounds and a distorted-octahedral structure for the copper(II) compounds.

In these structures, it is probable that four positions are used to form bonds to the carbonyl groups of two saccharin molecules and to the sulfonyl groups of two other saccharin molecules, while the remaining sulfonyl and carbonyl groups of each molecule interact with other metal ions to give a polymeric structure with a molar metal: saccharin ratio of 1 : 2. The remaining two octahedral positions not bound to the water (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 which stabilizes these compounds.

This phenomenon, together with the stronger carbonyl—metal and sulfonyl—metal interaction suggested by the IR spectra, explains the higher thermal stability of the anhydrous metal—saccharin compounds obtained from the complexes containing saccharin alone, with respect to the analogous systems obtained from the ternary complexes after the loss of the pyridine molecules.

Finally, comparing the initial decomposition temperatures of the anhydrous compounds of the series $(\mathrm{Msacc}_2) \cdot n\,\mathrm{H_2O}$ with the corresponding stability constants we find the following classical [5] trends:

Decomposition temperature Co(II) > Cu(II)
Stability constant Co(II) < Cu(II)

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