

**THERMAL BEHAVIOUR OF THE N-DONOR  
ADDUCTS OF METAL SACCHARINATES  
I. 2,2'-bipyridine saccharinato complexes of Co(II), Ni(II),  
Cu(II), Zn(II) and Pb(II)**

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**Abstract**

The adducts of Co, Ni, Cu, Zn and Pb saccharinates with 2,2'-bipyridine were synthesized and their thermal behaviour in the 20–1000°C temperature interval in a static air atmosphere was investigated. Regardless of the coordination, the decomposition starts with dehydration and proceeds with removal of the bipyridine ligand(s). The resulting metal(II) saccharinates adopt characteristic two-step decomposition, the first step being the SO<sub>2</sub> release. Their stability was found to be metal-dependent. The thermal decomposition pathways were correlated with the existing structural data about the compounds.

**Keywords:** 2,2'-bipyridine, N-donor adducts, saccharinates, thermal decomposition

**Introduction**

Some of the water-soluble salts (e.g., the Na, K, NH<sub>4</sub> and Ca salt) of saccharin (1,2-benzisothiazol-3(2H)-one 1,1-dioxide) are well known and widely used artificial sweeteners. However, the on-going dispute about the potential carcinogenic properties of saccharin has provoked much interest in the structural studies of saccharinato salts and complexes, as well as of their adducts. Besides the diffraction and spectroscopic studies, lately much effort has been also made to investigate the thermal behavior of such compounds in order to obtain additional structural information.

A brief chronological review of the existing literature data about the thermal properties of saccharinates are presented in continuation. Magri *et al.* [1] were first to describe the thermal decompositions of Co(sac)<sub>2</sub>·6H<sub>2</sub>O and Cu(sac)<sub>2</sub>·5H<sub>2</sub>O (hereafter

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*sac* denotes saccharinato ligand/ion, *py* and *bpy* stand for pyridine and 2,2'-bipyridine respectively), their pyridine adducts  $\text{Co(py)(sac)} \cdot x\text{H}_2\text{O}$  ( $x=1, 4$ ) and  $\text{Cu(py)}_2(\text{sac})_2 \cdot y\text{H}_2\text{O}$  ( $y=1, 2, 4$ ) [1] as well as of  $\text{Ni(sac)}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn(sac)}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn(py)}_2(\text{sac})_2 \cdot \text{H}_2\text{O}$  and  $\text{Ni(py)}_2(\text{sac})_2 \cdot 8\text{H}_2\text{O}$  [2]. The thermal behaviour in the temperature interval 303–623 K of Ni(II), Cu(II), Zn(II) and Cd(II) pyridine saccharinates was also reported later [3]. The decomposition of an oxovanadium(IV) complex described as a saccharin adduct was presented by Ferrer *et al.* [4]. In a brief paper [5], Yugeng reported some thermal data of  $\text{Cu(sac)}_2 \cdot 6\text{H}_2\text{O}$  and those of a mixed yttrium-copper ethanolate hydroxido complex. The thermoanalytical curves of  $\text{Zn(py)}_2(\text{sac})_2$  were discussed in connection with its crystal structure by Quinzani *et al.* [6]. Systematic reinvestigation of the thermal decompositions of the first transition row saccharinates of type  $[\text{M}(\text{H}_2\text{O})_4(\text{sac})_2] \cdot 2\text{H}_2\text{O}$  ( $M=\text{Mn, Fe, Co, Ni, Cu, Zn}$ ) together with a kinetic analysis of the dehydration process was undertaken by Içbudak *et al.* [7]. Lately, these authors also reported the thermal properties of the mixed hydrazine and ethylenediamine saccharinates of Co(II), Ni(II) and Cu(II) [8]. We [9] have recently presented data on the thermal decompositions of the pyridine saccharinates  $[\text{M}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$  ( $M=\text{Co}$  and  $\text{Ni}$ ) and  $[\text{Cu(sac)}_2(\text{H}_2\text{O})(\text{py})_2]$ . Very recently we have also investigated the thermal decomposition of all alkali saccharinates (except for the Li salt) [10].

Although the thermal data on saccharinates are less prevalent than the structural ones, they can sometimes be crucial for structural characterization. A representative example for such case is the structural investigation of copper(II) 2,2'-bipyridine saccharinato complex where thermal analysis data were resolving proof in formulating the compound as dihydrate [11].

In the present paper we report the results of the systematic study of the thermal decomposition of Co, Ni, Cu, Zn and Pb complexes with saccharin and 2,2'-bipyridine. The decomposition pathways of the complexes are discussed in connection with the available structural data from the diffraction and spectroscopic measurements.

#### *Structural data of 2,2'-bipyridine saccharinato complexes*

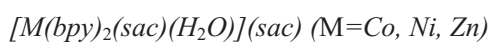
The isomorphous [12] 2,2'-bipyridine saccharinates of Mn(II) [13], Co(II) [14], Ni(II) and Zn(II) are monoclinic (space group  $P2_1/n$ ) and have the general formula  $[\text{M}(\text{bpy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$  ( $M=\text{Mn, Co, Ni}$  and  $\text{Zn}$ ). The crystal structure of a trihydrate Cu(II) complex,  $[\text{Cu}(\text{bpy})_2(\text{sac})](\text{sac}) \cdot 3\text{H}_2\text{O}$  [15], was reported simultaneously with the structure of a dihydrate,  $[\text{Cu}(\text{bpy})_2(\text{sac})](\text{sac}) \cdot 2\text{H}_2\text{O}$  [11]. Later considerations [16], however, revealed that it is very probable that the two crystal structures describe the same compound which is more likely to be a dihydrate (orthorhombic,  $C222_1$ ). The crystal structure of the Hg(II) adduct,  $[\text{Hg}(\text{bpy})(\text{sac})_2]$  (monoclinic,  $P2_1/c$ ), was also determined [17], and recently that of the Pb(II) complex  $[\text{Pb}(\text{bpy})(\text{sac})_2(\text{H}_2\text{O})]$  (monoclinic,  $P2_1/n$ ) has been published as well [18]. In addition, the crystal structure of a mixed oxalato 2,2'-bipyridine saccharinate of Cu(II) was also reported [19].

## Experimental

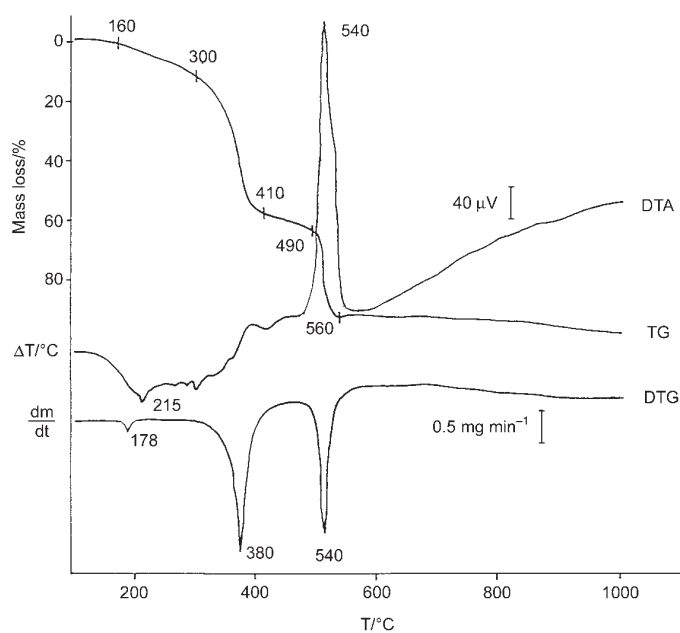
The complexes were prepared from the respective metal(II) acetates or carbonates, 2,2'-bipyridine and saccharin mixed in stoichiometric ratio. The DTA, TG and DTG studies were carried out on a Q Derivatograph MOM, Hungary, in a static air atmosphere using Pt crucibles. The temperature range was from ambient to approximately 1000°C. The samples weighed around 100 mg,  $\beta=10^{\circ}\text{C min}^{-1}$ .

## Results and discussion

The thermoanalytical curves of the studied complexes are shown in Figs 1–5. The corresponding thermal decomposition data are summarized in Table 1.



The isomorphous Co (Fig. 1), Ni (Fig. 2) and Zn (Fig. 3) bipyridine saccharinates adopt similar three-stage decomposition pathways and thus they will be discussed simultaneously.



**Fig. 1** TG, DTG and DTA curves of  $[\text{Co}(\text{bpy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$

The onset of the decomposition of the complexes is above 150°C with dehydration and immediate sublimation of the bipyridine. Small endothermic peaks (155, 195 and 215°C for Zn, Ni and Co complexes, respectively) accompanied with a group of

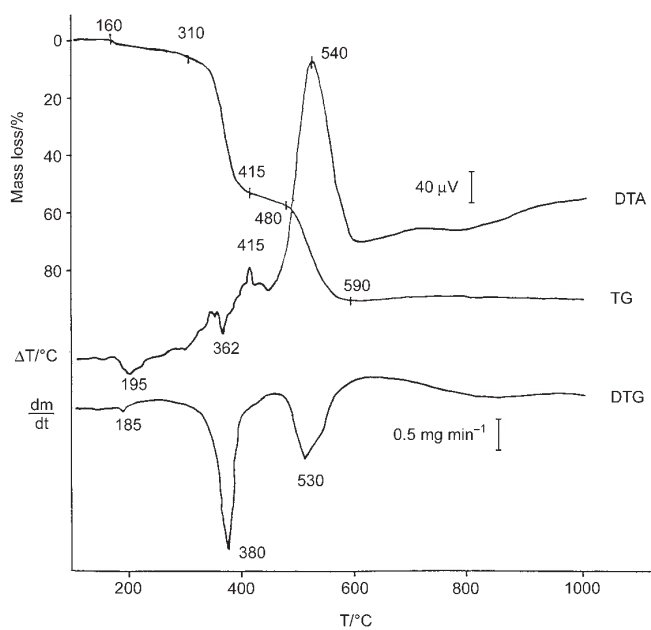


Fig. 2 TG, DTG and DTA curves of  $[\text{Ni}(\text{bpy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$

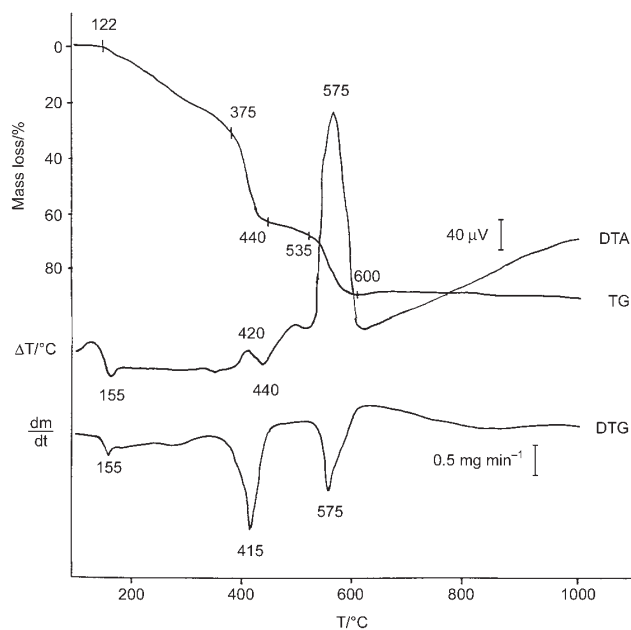


Fig. 3 TG, DTG and DTA curves of  $[\text{Zn}(\text{bpy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$

minor loosely defined endothermic effects appear on the DTA curve. Similar 'waved' shape of the thermoanalytical curves has been regularly obtained in case of removal of heavy *N*-donor aromatic molecules (e.g., pyridine, [20]). As can be seen from the TG curves, the processes of dehydration and debipyridination decomposition are satisfactorily resolved only in the case of the Ni complex, Fig. 2. By the end of this stage, the Zn complex has lost the largest portion of the bipyridine (Fig. 3), and the Ni complex the smallest.

During the second stage (Figs 1–3), the remaining bipyridine sublimes and, simultaneously, the saccharinato ligands decompose. On the bases of the mass losses (TG curves), it was supposed that both sulfoimide rings (Figs 1–3) liberate 2 moles of SO<sub>2</sub> per formula unit. Single DTG peaks correspond to these processes (380°C for Co and Ni, 415°C for Zn), while diffuse shape can be observed on the respective DTA curves.

The third stage (Figs 1–3) (starting at 460, 450 and 480°C in case of Co, Ni and Zn, respectively) represents complete decomposition of the saccharinato ligands, as shown by the pronounced exothermic effects, indicative for redox process (DTA maxima at 540°C for Co and Ni and 575°C for Zn; Figs 1–3). In the case of the Co complex, this process is especially vigorous and fast, leaving an empty crucible and a mass loss of practically 100%. The same factors are probably responsible for the greater value of the observed mass loss (94%) than the expected one for NiO (90.9%) or elementary Ni (92.2%) in the case of the decomposition of the Ni adduct. The final decomposition product of the Zn complex is black and has a metal shine and could be carbonaceous Zn (experimental mass loss 92.5%, calculated on Zn 91.4%). The exis-

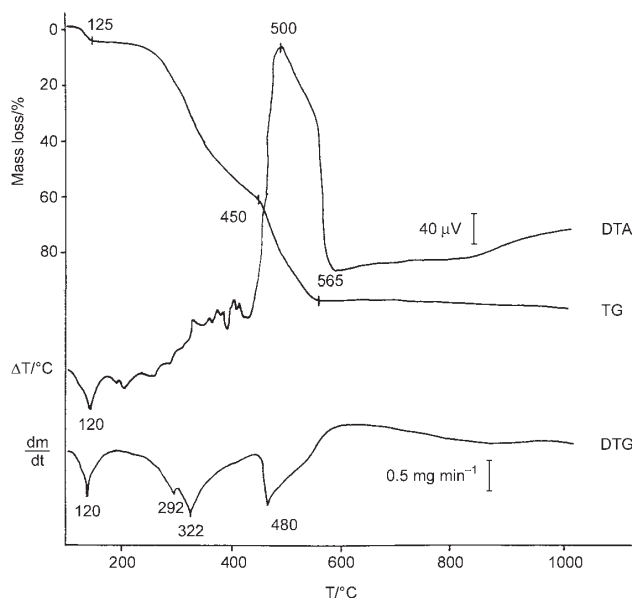
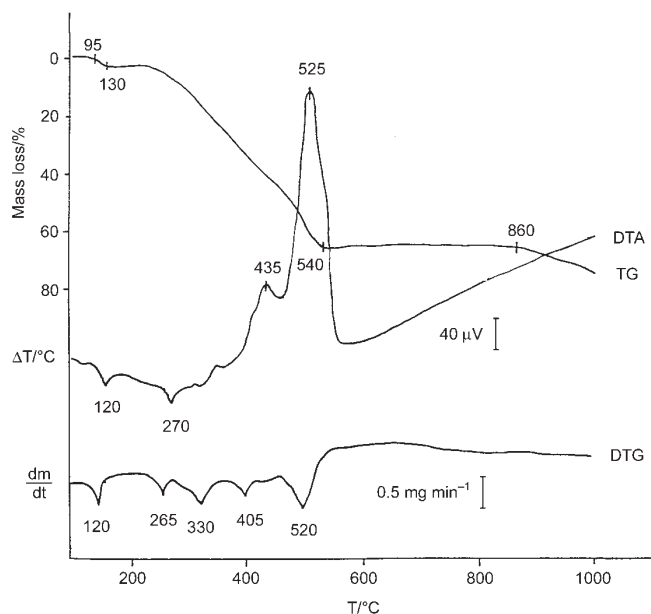


Fig. 4 TG, DTG and DTA curves of  $[\text{Cu}(\text{bpy})_2(\text{sac})](\text{sac}) \cdot 2\text{H}_2\text{O}$

tence of strong reducing environment in static air atmosphere containing abundant carbon after burning of the organic residue could result in the formation of carbonaceous metallic Ni or Zn, also noted by other authors [21], instead of the expected formation of the metal oxide in air atmosphere.

*[Cu(bpy)<sub>2</sub>(sac)](sac)·2H<sub>2</sub>O*

The one-step dehydration of the Cu complex (DTG peaks at 120°C, Fig. 4) starts and ends at much lower temperatures than the other studied complexes (Table 1). The experimentally found value of the water content (5%) is in good agreement with the calculated one (4.64%), supporting the data of Grupče *et al.* [16] that this compound is a dihydrate. The anhydrous complex exists in the 150–200°C interval. During the second stage, decomposition of the bipyridine ligands and both saccharinato ligands with release of SO<sub>2</sub> proceeds. The two steps could be only inspected via the pair of DTG peaks (292 and 322°C). The third stage is associated with vigorous and strong exothermic redox process (DTA peak at 500°C) which results in empty crucible and the total mass loss amounts around 100%. Similar behavior was noted in the case of other organo-metal compounds of copper [21]. The decomposition temperatures generally reveal that the Cu bipyridine saccharinato complex is less stable than the corresponding Co, Ni or Zn complexes (compare Figs 1, 2 and 3 with Fig. 4).



**Fig. 5** TG, DTG and DTA curves of  $[\text{Pb}(\text{bpy})(\text{sac})_2(\text{H}_2\text{O})]$

*[Pb(bpy)(sac)<sub>2</sub>(H<sub>2</sub>O)]*

As expected from the distinctively different molecular structure [18], the decomposition pathway of the Pb complex (Fig. 5) is pronouncedly different from the rest of the other studied compounds (Figs 1–4).

**Table 1** Thermal decomposition data for 2,2'-bipyridine saccharinates of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II)

	Temperature range/°C	DTA <sub>max</sub> /°C	Removed species	Mass loss/%		Observed total mass loss/%
				observed	calculated	
<i>[Co(bpy)<sub>2</sub>(sac)(H<sub>2</sub>O)](sac)</i>						
1	160–220	215(–)	H <sub>2</sub> O	2.5	2.39	
2	220–450	c(–),415(+)	2bpy, 2SO <sub>2</sub>	59.5	58.44	
3	460–550 700–1000	540(+)	undefined	31.0		100
<i>[Ni(bpy)<sub>2</sub>(sac)(H<sub>2</sub>O)](sac)</i>						
1	160–220	195(–)	H <sub>2</sub> O	2.5	2.39	
2	310–460	c(–),415(+)	2bpy, 2SO <sub>2</sub>	58.0	58.46	
3	450–590	540(+)	undefined	33.0		94
<i>[Zn(bpy)<sub>2</sub>(sac)(H<sub>2</sub>O)](sac)</i>						
1	152–180 180–375	155(–)	H <sub>2</sub> O bpy	3.0 21.5	2.37 20.55	
2	375–440	c(–),420(+)	bpy, 2SO <sub>2</sub>	40.5	37.41	
3	480–600	575(+)	undefined	27.0		92.5
<i>[Cu(bpy)<sub>2</sub>(sac)](sac)·2H<sub>2</sub>O</i>						
1	86–127	120(–)	2H <sub>2</sub> O	5.0	4.64	
2	200–450	c(–)	2bpy, 2SO <sub>2</sub>	57.0	56.75	
3	450–565	500(+)	undefined	38.0		100
<i>[Pb(bpy)(sac)<sub>2</sub>(H<sub>2</sub>O)]</i>						
1	97–130 240–360	120(–) 270(–)	H <sub>2</sub> O bpy	3.0 22.0	2.42 20.94	
2	~360–450	435(+)	2SO <sub>2</sub>	17.0	17.18	
3	450–540 860–1000	525(+)	undefined	33.0		66 75

<sup>a</sup>Symbols denote: (+) – exothermic, (–) – endothermic, c – complex

The dehydration of the Pb complex is performed in one step with a single endothermic peak during the first stage, at relatively low temperature (DTG and DTA

peaks at 120°C). The anhydrous saccharinate is stable up to about 240°C and afterwards decomposes without differentiation of the involved processes. As a result, a descending continuous TG curve is obtained. In some sense this is consistent with the molecular structure of this compound [18] represented by a network of hydrogen bonded and coordinated ligands and  $\text{Pb}^{2+}$  ions, rather than from discrete formula units. As many as four DTG peaks could be resolved (Fig. 5, Table 1) within this complex process. The first two DTG peaks (at 265 and 330°C) are probably in connection with the release of the bipyridine molecules, which is supported by the irregular shape of the DTA curve in this region. The last two DTG peaks correspond to the two DTA peaks of different intensity (at 435 and 525°C) and can be identified as peaks corresponding to the decomposition of  $\text{Pb}(\text{sac})_2$ . On the basis of these considerations, the approximate temperature regions of the release of 2,2'-bipyridine and the saccharinato decomposition product are estimated (Table 1). From the observed mass loss at 540°C (about 66%; theoretically calculated on elementary Pb 72.3%), it can be concluded that the residue is a mixture of Pb and carbon rather than pure metallic lead, in agreement with some earlier observations [21] as well as with the above given explanation for the Ni and Zn complexes. Starting from 860°C the residual carbon is slowly oxidized, and the final mass loss is 75%, close to the expected value confirming the above presumptions.

## Conclusions

The decomposition pathways of the adducts of the Co, Ni and Zn saccharinates with 2,2'-bipyridine are similar, but at the same time different from the ones of Cu and Pb complexes. The dehydrated and debipyridinated saccharinates adopt the characteristic two-step decomposition, during the first step of which  $\text{SO}_2$  is released. Their stability was found to be metal-dependent. Strong reducing environment formed after burning of the saccharinato ligands in static air atmosphere induces formation of carbonaceous metals in some cases.

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