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THERMAL BEHAVIOUR OF THE *N*-DONOR ADDUCTS OF METAL SACCHARINATES

III. Imidazole saccharinates of Co(II), Ni(II) and Cd(II)[*]

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Abstract

The complexes $[M(HIm)_4(H_2O)_2](sac)_2$ (*M*=Co, Ni) and $[Cd(HIm)_2(sac)_2]_2$ with saccharin (sac) and imidazole (HIm) were synthesized and their thermal (TG, DTG and DTA) behaviour in the interval from room temperature up to 1000°C in a static air atmosphere was investigated. Irrespectively of whether the deprotonated saccharinato residues are present as ligands or ions or both as ligands and ions, the anhydrous complexes regularly decompose in two stages. The thermal data of 16 saccharinato complexes (including the title compounds) were correlated with the respective structural data. The general thermal stability order of the saccharinato complexes can be represented as: Pb(II)<Zn(II)<Co(II)≤Ni(II)<Cd(II) (the stability of the Cu saccharinates depends on the particular compound) and is dictated by several structural factors, e.g. metal ionic radii, participation of the water in the coordination sphere of the metal and other structural characteristics.

Keywords: *N*-donor aromatic adducts, saccharinates, thermal decomposition

Introduction

The water-soluble alkali and earth-alkali salts of the *o*-benzoic sulfimide known as saccharin (systematic name: 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide) have received wide commercial application as artificial sweetening agents. The latest renewal of the discussions about the potential carcinogenic properties of the parent sulfimide, however, has invoked large interest in the structural studies of the saccharinates of various metals. Within the on-going structural, spectroscopic and thermal studies of saccharinates, we have been interested in the structural properties

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[*] For the second part of this series, see: P. Naumov, O. Grupče, V. Jordanovska, B. Boyanov, G. Jovanovski, Thermal behaviour of the *N*-donor adducts of metal saccharinates. II. 1,10-Phenanthroline saccharinato complexes of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), J. Therm. Anal. Cal., 65 (2001) 871.

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of the adducts of saccharinates with various mono- or polymembered aromatic *N*-donor bases (e.g., imidazole, pyridine, 2,2'-bipyiridine and 1,10-phenanthroline).

Our extensive literature research for thermal data on saccharinates revealed that they are yet not extensive compared to the corresponding structural data. Up to now, the thermal behaviour of the following compounds was investigated: saccharinates and the pyridine saccharinates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) [1–3], oxovanadium(IV) saccharinato complex [4], $Cu(sac)_2{\cdot}6H_2O$ and a mixed YCu ethanolate hydroxido complex [5], $Zn(py)_2(sac)_2$ [6], the first transition row saccharinates of type $[M(H_2O)_4(sac)_2]{\cdot}2H_2O$ (*M*=Mn, Fe, Co, Ni, Cu, Zn) [7], hydrazine and ethylenediamine saccharinates of Co(II), Ni(II) and Cu(II) [8]. We have recently presented data on the thermal decompositions of the Co(II), Ni(II) and Cu(II) pyridine [9], Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) 2,2'-bipyridine [10] and Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) 1,10-phenanthroline [11] saccharinates. We have also investigated the thermal decomposition of all alkali saccharinates (except for the Li salt) [12].

In the present paper we report the results from the thermal (TG, DTG and DTA) study of the thermal decomposition of Co(II), Ni(II) and Cd(II) complexes with saccharin and imidazole as well as the results of the systematic analysis of thermal data of saccharinato aromatic *N*-adducts. The decomposition pathways of the complexes are discussed in connection with the respective structural and the infrared data.

Structural data about the complexes

The crystal structure determination of Co(II) [13] and Ni(II) [14] complexes revealed that these compounds are isomorphous, belonging to the P group of the triclinic system. The structures are composed of saccharinato anions and metal cations, the latter being octahedrally coordinated by four imidazole molecules and two *trans*-water molecules. The infrared data of the complexes are recently investigated [15].

Cd(II) complex (monoclinic, C2/c, Z=4) [16] has a dimeric structure composed of $[Cd(HIm)_2(sac)_2]_2$ moieties. Two saccharinato ligands as well as two imidazole molecules of the monomeric unit are coordinated to the metal atom through their nitrogen atoms, forming a trigonal bipyramid with the imidazole nitrogen atoms on the apexes. While one saccharinato ligand of each monomeric unit is *N*-monodentate, the other *N*-coordinated saccharinato ligand uses its carbonyl oxygen to coordinate to the Cd atom of the other monomer, acting as an amidato-like bridging ligand. Thereby nearly planar centrosymmetric octagonal ring Cd–N–C–O–Cd'–N'–C'–O' is formed. The IR spectroscopic data of the complex are also reported [17].

Experimental

The complexes were prepared from aqueous solutions of the respective metal(II) acetates, imidazole and saccharin, mixed in stoichiometric ratio. DTA and TG studies were carried out on a Q derivatograph (MOM) in static air atmosphere using Pt crucibles, in the temperature range from room temperature to approximately 1000°C. The mass of the samples was 50 mg, β=10°C min^{-1}.

Results and discussion

The thermoanalytical curves of the complexes are shown in Figs 1–3. The corresponding numerical data are summarized in Table 1.

$[Co(HIm)_4(H_2O)_2](sac)_2$

The decomposition of Co(II) compound (Fig. 1) consists of three stages. During the first stage (103–290°C) the complex is dehydrated in one step (a single peak on the DTG curve and an endothermic DTA peak at about 109°C). This is consistent with the existence of a single structural type of water molecules in the structure. Further heating causes slow sublimation of one of the coordinated imidazole molecules, resulting in a diffuse appearance of the DTA curve and a small descending slope on the

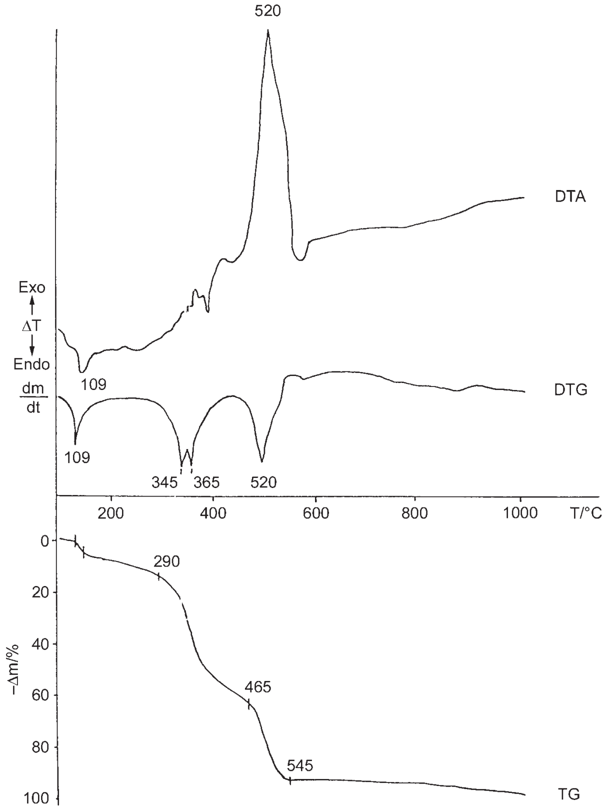

Fig. 1 Thermoanalytical curves of $[Co(HIm)_4(H_2O)_2](sac)_2$

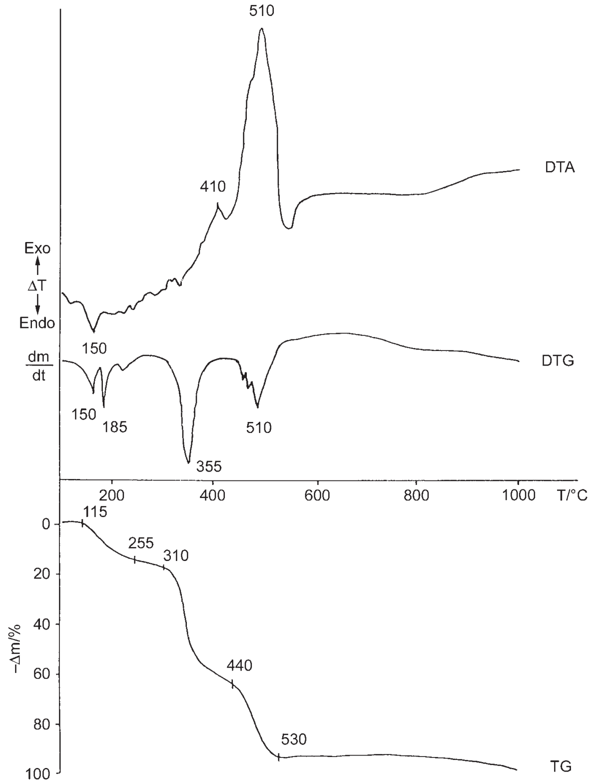

Fig. 2 Thermoanalytical curves of $[Ni(HIm)_4(H_2O)_2](sac)_2$

TG curve. This is a confirmation that the imidazole ligands are not structurally equal. At about 290°C one molecule of imidazole is already released, as inferred by the agreement between the theoretical and the experimental value for the mass loss (Table 1). The resulting structure is very unstable and during the second stage (from 290°C) it undergoes immediate decomposition by release of the remaining imidazole ligands. Consequently, the decomposition of the saccharinato ligand starts with the release of two SO_2 molecules. Two DTG peaks (at about 345 and 365°C) correspond to these parallel processes (Fig. 1). During the third stage, the residue decomposes vigorously, followed by a strong exothermic DTA peak at 520°C implying the redox nature of this process. The decomposition of $Co(sac)_2$ in the present case, therefore, adopts the pathway proposed for $Co(sac)_2$, $Ni(sac)_2$ and $Cu(sac)_2$ in a static air atmosphere [9]. According to the mass loss alone, it is not possible to determine the final product. One possible explanation is that the vigorous redox reaction practically empties the crucible, and the remaining carbon is slowly oxidized, as it was previously observed in the case of other metal-organic compounds [18].

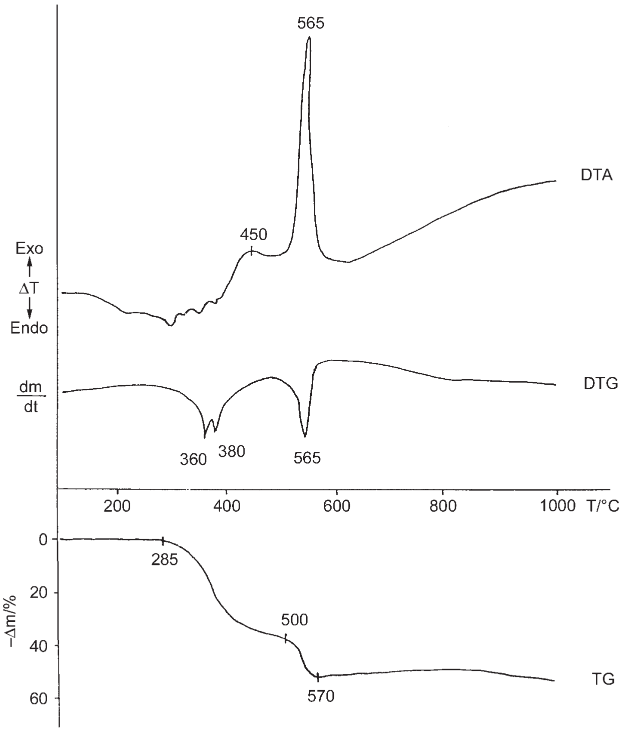

Fig. 3 Thermoanalytical curves of $[Cd_2(HIm)_4(sac)_4]$

Table 1 Thermal decomposition data for imidazole saccharinates of Co(II), Ni(II) and Cd(II)

	Temperature range/°C	Removed species	Mass loss/%		Product
			observed	calculated	
$[Co(HIm)_4(H_2O)_2](sac)_2$					
1	103–135	$2H_2O$	5	4.92	$Co(HIm)_4(sac)_2$
	135–290	HIm	9	9.30	$Co(HIm)_3(sac)_2$
2	290–455	3HIm, $2SO_2$	46	45.41	$Co(C_6H_4CON)_2$
3	465–545		32	30.08	See text
$[Ni(HIm)_4(H_2O)_2](sac)_2$					
1	119-255	$2H_2O$, HIm	14	14.22	$Ni(HIm)_3(sac)_2$
2	310–430	3HIm, $2SO_2$	46	45.42	$Ni(C_6H_4CON)_2$
3	440–530		31	30.09	See text
$[Cd_2(HIm)_4(sac)_4]$					
1	285–450	4HIm, $4SO_2$	44	43.12	$Cd_2(C_6H_4CON)_4$
2	500–570		34	35.90	CdO

$[Ni(HIm)_4(H_2O)_2](sac)_2$

Although the thermal decomposition of the Ni(II) complex (Fig. 2) is similar with that of the isomorphous Co(II) compound (Fig. 1), some differences are also present. Strong difference in the thermal decomposition pathways was previously observed in the case of the isomorphous Co(II) and Ni(II)pyridine saccharinates as well [9].

The first stage of the thermal decomposition of Ni(II) imidazole saccharinate starts at about 115°C with the release of the water and one imidazole molecule in two steps (two DTG peaks at about 150 and 185°C; Fig. 2). According to the initial decomposition temperatures (Table 1), the stability of Ni complex is higher than that of the Co compound i.e. the water molecules in Ni(II) complex are also equal and more strongly bound. This is opposite of what was found for the respective pyridine adducts [9]. However, in contrast with the pyridine saccharinates, all water molecules in the present structures are coordinated [13, 14], which might be one of the reasons for the reversed order of stability. In contrast with the Co complex, the release of the first imidazole molecule takes place in a shorter temperature interval. Expectedly, only weak thermal effects are present on the DTA curve. After 310°C the residue loses the rest of the imidazole ligands and SO_2 from the saccharinato ions within a single step (one DTG maximum at 355°C). The remaining saccharinato residue burns vigorously in the last stage, accompanied with a strong exothermic peak (about 510°C) and a smaller one (about 410°C). This process is over at about 530°C. The TG curve then shows a horizontal, but probably due to oxidation of the remaining carbon, after 830°C it slowly declines, accompanied with an exotherm DTA effect. The thermal decomposition probably ends with emptying of the crucible, as it is known for other metal-organic compounds.

$[Cd_2(HIm)_4(sac)_4]$

Understandably, due to the absence of crystal water, Cd(II) complex is the most stable of all investigated imidazole complexes (Table 1). The compound shows two-stage decomposition (Fig. 3), different from those of the Co(II) and Ni(II) complexes. The first stage (from 285 to about 450°C) is complex and involves two processes (two DTG peaks): release of all four imidazole molecules and, subsequently, of SO_2 from each saccharinato ligand. Accordingly, two DTG peaks (360 and 380°C) and a diffuse appearance of the DTA curve are present. During the second stage (from about 450°C onwards), the remaining metal-organic residue is decomposed, corresponding to a strong exothermic peak (DTA maximum at 565°C), indicative for a redox process. The low resolution of the two stages leads to the inability to obtain more accurate experimental values for the respective mass losses. According to the mass loss (Table 1) and the earlier data [18], the final product is CdO.

Systematic analysis of the thermal data for the aromatic N-adducts of metal(II) saccharinates

The present data, together with the previous results [9–11] obtained under the same experimental conditions (instrument, method[***] etc.) as in this study, enable systematic study of the thermal behaviour of the aromatic *N*-adducts of metal(II) saccharinates. Overall of 16 complexes of imidazole (3), pyridine (3), 2,2'-bipyridine (5) and 1,10-phenanthroline (5) were accounted for.

The decomposition of all compounds starts with (partial or complete) dehydration, occasionally accompanied by the release of some of the ligands. The initial decomposition temperatures, taken as a measure of the thermal stability of the corresponding compounds showed rather regular trend within each class. The stability was as it follows:

Imidazole complexes: Co(II)<Ni(II)<Cd(II)
Pyridine complexes: Co(II)<Ni(II)<Cu(II)
2,2'-Bipyridine complexes: Cu(II)<Pb(II)<Zn(II)<Co(II)=Ni(II)
1,10-Phenanthroline complexes: Pb(II)<Zn(II)<Co(II)<Ni(II)<Cu(II)

The general order of thermal stability of the saccharinato complexes, therefore, can be represented as: Pb(II)<Zn(II)<Co(II)≤Ni(II)<Cd(II). The position of the Cu(II) saccharinates in the thermal stability order depends on the particular compound. The particular values of the temperatures of initial decomposition, however, are largely influenced by the respective structures and thus can not be compared directly. One additional factor are surely the relative ionic radii of the metal ions [7]. Eventual participation of the water in the coordination sphere of the metal also contributes to the stability of the complex. As an illustration to this, the series of structurally characterized pyridine and 2,2'-bipyridine complexes can be considered: the Cu(II) member is the only one with solely coordinated water within the first series, while the Cu(II) member in the latter series is the only member with non-coordinated water. Accordingly, the stability of Cu(II) pyridine saccharinate is the highest in its series, while that of Cu(II) 2,2'-bipyridine saccharinate is the lowest within the series of the bipyridine saccharinates.

Irrespectively of whether the saccharinato residues are present as ligands or ions or both as ligands and ions, in oxidizing static air atmosphere the saccharinato ligands/ions regularly decompose in two steps. The comparisons between the theoretical and experimental mass losses from the present study confirm the earlier suggestions [9] that during the first step SO_2 is released. This process is weakly exothermic and the accompanying temperature effect is sometimes precluded by the effects due to the release of other ligands. The corresponding DTA peak is found in the 330–500°C interval (mostly around 415°C), but due to the above reasons, sometimes might not be observed (especially in the case of Cu(II) compounds). The residue after this step can be described as $M(C_6H_4CON)_2$. During the second, strongly exothermic

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[***] One relevant difference might be only that the heating rate in [9] was lower (5°C min^{-1}).

process, the organic residue is burnt and generally, a carbonaceous product is obtained. The peak corresponding to the second decomposition step was observed in the 415–585°C range, but most frequently around 520°C. No straightforward correlation was observed between the participation of the deprotonated saccharin in the coordination sphere and the initial decomposition temperature of the saccharinato residues. However, the lowest temperature DTA peaks of the second decomposition step of the saccharinato residues were found for Cu(II) compounds, while the highest were those for Zn(II) and Cd(II) compounds.

Conclusions

The decomposition of the aromatic *N*-donor adducts of saccharinates starts with dehydration, accompanied or followed by loss of the molecules of the base. The general thermal stability order of the saccharinato complexes can be represented as: Pb(II)<Zn(II)<Co(II)≤Ni(II)<Cd(II) (the stability of the Cu saccharinates depends on the particular compound) and is being dictated by several structural factors, e.g. metal ionic radii, participation of the water in the coordination sphere of the metal and other characteristics of the particular structure. Irrespectively of whether the saccharinato residues are present as ligands or ions or both as ligands and ions, in oxidizing static air atmosphere the saccharinato ligands/ions regularly decompose in two steps.

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