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DECOMPOSITION PATHWAY OF DIAQUABIS(N,N'-DIMETHYL-1,2-ETHANEDIAMINE)Ni(II) ACESULFAMATE
Thermal and mass spectroscopic data

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Prediction of the thermal decomposition pathway of the metal complexes is very important from the theoretical and experimental point of view to determine the properties and structural differences of complexes. In the prediction of the decomposition pathways of complexes, besides the thermal analysis techniques, some ancillary techniques e.g. mass spectroscopy is also used in recent years. In the light of the molecular structures and fragmentation components, it is believed that the thermal decomposition pathway of most molecules is similar to the ionisation mechanism occurring in the mass spectrometer ionisation process. In this study, the thermal decomposition pathway of $[Ni(dmen)_2(H_2O)_2](acs)_2$ complex have been predicted by the help of thermal analysis data (TG, DTG and DTA) and mass spectroscopic fragmentation pattern. The complex was decomposed in four stages: a) dehydration between 84–132ºC, b) loss of N,N'-dimethylethylenediamine (*dmen*) ligand, c) decomposition of remained *dmen* and acesulfamato (*acs*) by releasing SO_2, d) burning of the organic residue to resulting in NiO. The volatile products observed in the thermal decomposition process were also observed in the mass spectrometer ionisation process except molecular peak and it was concluded that the ionisation and thermal decomposition pathway of the complex resembles each other.

Keywords: *acesulfamate, diamine, mass spectroscopy, Ni(II) complex, thermal decomposition*

Introduction

Acesulfame or acetosulfam ($C_4H_5SO_4N$, H*acs*) is an oxathiazinone dioxide and chemically named as 6-methyl-1,2,3-oxathiazin-4(3H)-one 2,2-dioxide; 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-one 2,2-dioxide. It was discovered by Clauss [1] in 1967 and widely used as an artificial sweetener [2] since 1988 after FDA (Food and Drug Administration) approval. More than 30 countries have approved the use of acesulfame-K, in soft drinks, candies, toothpastes, mouthwashes cosmetics and pharmacological products [3]. Acesulfame has no calories and it is not digested, accumulated, and changed in the human metabolism and discharged quickly from the body [2]. Chemistry of the metal-artificial sweetener complexes is an interesting area of research because of the potential biological significance of such compounds. There have been many studies on coordination complexes, especially with the first-row transition metals [4–11]. Chemically, it bears some structural resemblance to saccharine (Fig. 1). The acesulfamate ion ($C_4H_4NO_4S^-$, *acs*) has several potential donor atoms, i.e. the imino nitrogen, one carbonyl and two sulphonyl oxygens, which may be utilized in forming coordination bonds with different metal ions. On the other hand, the acesulfamate ions may remain outside the coordination sphere when the secondary ligand having strong chelating properties. The spectroscopic and thermal properties of a number of amine complexes containing saccharinate as a counter ion have been studied by the researchers extensively in the last two decades [6, 8, 12–14]. In the prediction of the decomposition pathways, besides the thermal analysis techniques, some ancillary techniques e.g. mass spectroscopy is also used in recent years [15–17]. In this study, the thermal decomposition pathway of $[Ni(dmen)_2(H_2O)_2](acs)_2$ complex have been predicted by the help of thermal analysis data (TG, DTG and DTA) and mass spectroscopic fragmentation pattern. The investigated complex is the first reported example of amine complexes containing acesulfamate as a counter ion among several new complexes synthesised in this laboratory.

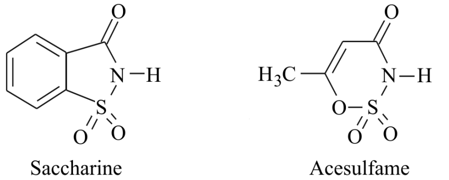

Fig. 1 The molecular structure of acesulfame and saccharine

Experimental

Materials and instrumentation

A Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser was used to record

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simultaneous TG, DTG and DTA curves. The experiments were performed in static air atmosphere with a heating rate of 10 K min^{-1} from room temperature to 1000°C in platinum crucibles. The samples were weighed approximately 10 mg and in DTA measurement highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity setting was a 0.05 mg s^{-1}. The elemental and mass spectroscopic analysis was carried out in TUBITAK Marmara Research Institute of Turkey. Mass spectroscopic analysis was performed on a Fisons MD 800 mass spectrometer coupled to a Fisons 8000 GC and FAB ionisation source. IR spectrum was recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FTIR spectrophotometer using KBr pellets to determine the identity of the final products.

Synthesis of [Ni(dmen)$_2$(H$_2$O)$_2$](acs)$_2$

0.455 g (1 mmol) of $Ni(acs)_2(H_2O)_4$ was dissolved in 50 mL methanol and a 0.176 g (2 mmol) N,N'-dimethylethylenediamine (*dmen*) in 50 mL methanol was added on to the stirred solution. Mixture was further stirred for 2 h at 50°C temperature and then cooled to ambient temperature. The formed violet crystals were washed with methanol and dried under vacuum. Yield was 93.00%. Elemental analysis data: found (calcd): C: 32.27% (32.24%), H: 6.27% (6.05%), N: 13.53% (14.11%).

Results and discussion

Thermal analysis of [Ni(dmen)$_2$(H$_2$O)$_2$](acs)$_2$

The superimposed thermal analysis curves (TG-DTG and DTA) of the complex are given in Fig. 2. In the first stage, dehydration of the complex occurs at 84–132°C temperature intervals and 2 moles of aqua ligands removed (found: 6.2%; calculated: 6.1%). The originally violet colour of the complex changes to blue on dehydration. Following the dehydration, the resulted $[Ni(dmen)_2](acs)_2$ anhydrous complex remained stable up to 217°C. The formation of two different new compounds is possible following the loss of the coordinated water from $[Ni(dmen)_2(H_2O)_2](acs)_2$. (I) the coordination number of Ni(II) may be reduced from 6 to 4 by the loss of aqua ligands giving a square-planar complex of $[Ni(dmen)_2](acs)_2$ or (II) $[Ni(dmen)_2(acs)](acs)$ complex may be formed by the addition of counter ion (*acs*) to the coordination sphere as given below.

$$[Ni(dmen)_2(H_2O)_2](acs)_2 \rightarrow [Ni(dmen)_2](acs)_2 + 2H_2O \quad (84\text{–}132^\circ C) \tag{I}$$

$$[Ni(dmen)_2(H_2O)_2](acs)_2 \rightarrow \rightarrow [Ni(dmen)_2(acs)](acs) + 2H_2O \quad (84\text{–}132^\circ C) \tag{II}$$

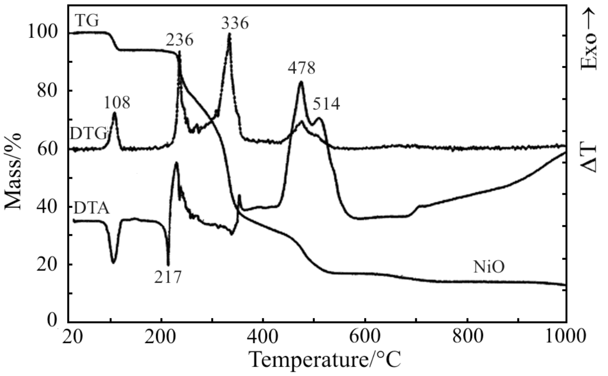

Fig. 2 TG, DTG and DTA curves of $[Ni(dmen)_2(H_2O)_2](acs)_2$

If a square plane $[Ni(dmen)_2](acs)_2$ complex (I) had been formed, it would have been a diamagnetic one. But, the formation of a paramagnetic compound (μ_{eff}=2.78 B.M.) after the loss of aqua ligands may prove that a $[Ni(dmen)_2(acs)](acs)$ complex (II) was likely to be formed. The addition of counter ions to the coordination sphere was also observed in the previously reported studies as given below [6, 15].

$$[Cr(en)_3]Cl_3 \rightarrow cis\text{-}[Cr(en)_2Cl_2]Cl + en \quad (260^\circ C) \tag{I}$$

$$[Cr(en)_3](SCN)_3 \rightarrow trans\text{-}[Cr(en)_2(SCN)_2]SCN + en \quad (190^\circ C) \tag{II}$$

$$[Cu(dmen)_2(H_2O)_2](sac)_2 \rightarrow \rightarrow [Cu(dmen)_2(sac)](sac) + 2H_2O \quad (74\text{–}125^\circ C) \tag{III}$$

On the other hand, the formation of $[Ni(dmen)_2(acs)](acs)$ complex occurs only in the solid state by thermal decomposition, otherwise impossible to synthesis such a complex in aqueous media. Thus, the thermal decomposition process itself may be utilised as a solid phase synthesis method for some kind of compounds. At 217°C the melting accompanied with decomposition begins. In the second stage, being exothermic, a mole of *dmen* ligand was released from the molecule at 217–260°C temperature intervals (found: 15.4%; calculated: 14.9%). The blue colour of the anhydrous complex changes to dark green colour by the removal of *dmen* ligand. The neutral ligands present in the coordination sphere such as ethylenediamine and N,N'-dimethylethylenediamine also are released by an exothermic reaction [18]. In the third stage, the other *dmen* ligand and acesulfamate ion starts to decompose at 279–368°C temperature intervals. In the decomposition of acesulfamate, SO_2 is likely to be produced. The observed exothermic stage may also be the strong proof of the releasing of SO_2, because inversion of SO_2 to SO_3 in static air atmosphere is an exothermic phenomenon. In the literature, the metal-saccharine complexes with similar structure are also said to be decomposed by releas-

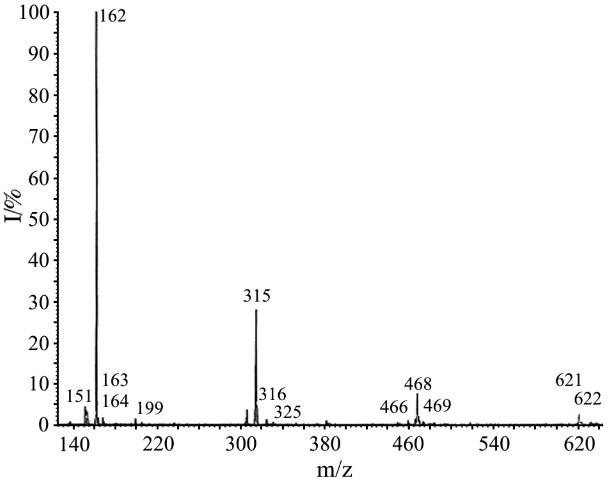

Fig. 3 The mass spectrum of $[Ni(dmen)_2(H_2O)_2](acs)_2$

ing of SO_2 [19, 20]. The organic residues formed by the partial decompositions of ligands were burnt in the excessive exothermic stage (DTA_{max}: 478, 514°C) corresponding to 427–578°C temperature intervals. The final decomposition product, namely NiO, was identified by IR spectroscopy with the corresponding spectrum obtained under the same condition as the pure NiO.

Analysis of the mass spectrum of $[Ni(dmen)_2(H_2O)_2](acs)_2$

As it is well known that the mass spectrum of any substance mainly reveals the most delicate and fragile points present in the structure of a molecule. It was assumed that the thermal process somewhat resembles the ionisation process since breaking of the chemical bonds need almost the same amount of energy. Therefore, analysing the mass spectrum of any substance may assist in predicting of more accurate identities or at least controlling the correctness of the identity of the thermal decomposition products by comparing with the ionisation fragments up to some degree [21, 22]. For this purposes, the mass spectrum of $[Ni(dmen)_2(H_2O)_2](acs)_2$ complex were recorded to establish a relation between the thermal and ionisation process to predict more appropriate thermal decomposition pathway. The mass spectrum recorded by FAB technique is given in Fig. 3.

In some situations, the mass spectra of the organic or organic part containing compounds may become very complicated with a complex fragmentation pattern [17]. Therefore, in the evaluation of mass spectra, decomposition products whose peak size is small were generally neglected for the sake of simplicity at the first step. As may be seen from the Fig. 3 that the mass spectrum of $[Ni(dmen)_2(H_2O)_2](acs)_2$ complex is not very complicated and only the major peaks, which were produced in significant quantities in the process were appeared. In addition to this, no molecular peak was observed. The relative abundance of the fragments produced is related to the strength and the chemical nature of the bonds that held the fragments to the rest of the molecules and shows the likely break up points. Absence of the molecular peak may indicate that almost 100% of the molecular ion is decomposed in the ionisation process. Predicting the identity of the mass spectroscopic fragments may help to explain the formation of the suggested products that were later obtained in the experimental decomposition process. For example, the peak observed at *m*/*z*=468 is possibly corresponds to $[Ni(dmen)](acs)_2$ molecule produced by the loss of two moles of water molecules and one mole of *dmen* molecule from $[Ni(dmen)_2(H_2O)_2](acs)_2$ molecule in the ionisation process. Formation of this fragments in the thermal process may also be proved by the thermal analysis data, since the formation of $[Ni(dmen)](acs)_2$ was observed by the loss of two moles of aqua ligands at 84–132°C temperature intervals (found: 6.2%; calculated: 6.1%) and one mole of *dmen* ligand at 217–260°C temperature intervals (found: 15.4%; calculated: 14.9%). The compound, $[Ni(acs)_2]$, formed

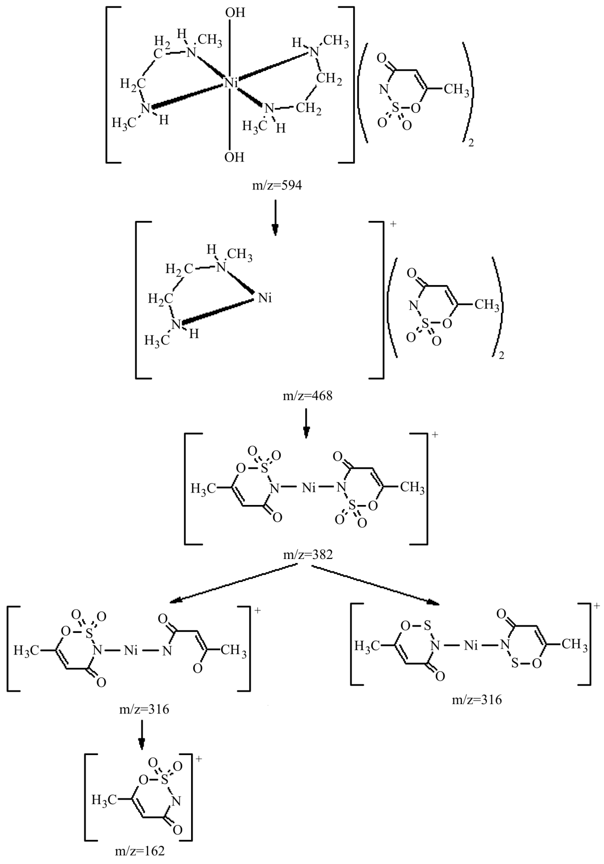

Fig. 4 Mass spectral fragmentation pattern of $[Ni(dmen)_2(H_2O)_2](acs)_2$

by the loss of other *dmen* ligand from [Ni(dmen)](acs)$_2$ and an intermediate compound is formed from [Ni(acs)$_2$] by the release of one mole SO$_2$ were observed in the mass spectrum at m/z=383 and m/z=316 values, respectively (Fig. 4). This may confirm that acesulfamate ion is thermally decomposed by the release of SO$_2$ as it was previously mentioned. The possible decomposition products of [Ni(dmen)$_2$(H$_2$O)$_2$](acs)$_2$ complex observed in the ionisation process are given in Fig. 4. The observed ionisation products somewhat resembles the products predicted by the thermal analysis results.

Conclusions

Prediction of the thermal decomposition pathway of the metal complexes is very important from the theoretical and experimental respects to determine the properties and structural differences effectively. Besides the thermal analysis techniques, some ancillary techniques e.g. gas chromatography, mass spectroscopy are also used in the prediction of the decomposition pathway in recent years. In this study, the thermal decomposition pathway of [Ni(dmen)$_2$(H$_2$O)$_2$](acs)$_2$ complex have been predicted by the help of thermal analysis (TG, DTG and DTA) and mass spectroscopic data simultaneously. The results of the thermal and mass spectroscopic analysis of [Ni(dmen)$_2$(H$_2$O)$_2$](acs)$_2$ complex show strong agreement for the observed products and a relation between the thermal and ionisation process may be established to predict more accurate decomposition pathway. It may be concluded that the thermal analysis and mass spectroscopic ionisation process are somewhat similar in many respects and may be utilised in the more sensible prediction of the thermal decomposition pathway of the metal complexes.

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