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Novel Al(III) and In(III) complexes containing acesulfame and nicotinamide/*N,N*-diethylnicotinamide ligands. Synthesis and structural characterization

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Abstract

Single-ligand (acesulfame) and mixed-ligand (acesulfame-nicotinamide/N,N-diethylnicotinamide) complexes of Aluminum (Al) and Indium (In) metal cations with 3+ oxidation steps in the 3A group, called earth metals, were synthesized and their structural characterizations were examined. The chemical compositions of the complexes were investigated by elemental analysis method, their binding properties by infrared and solid state UV-Vis spectroscopy, their degradation products analysis by GC-MS spectroscopy and their thermal behavior by TGA/DTA/DrTGA analysis. Acesulfame molecule, which is frequently used in industry, especially as an artificial sweetener, attracts attention as a valuable ligand in terms of coordination chemistry, thanks to the many electron-donating active groups it contains. It is also an easy ligand to work with, as it can form solids by precipitating to obtain a single crystal in coordination compounds. Although complex structures with transition metals are frequently found in the literature, studies on earth elements have not yet been found. It is important that the studies to be carried out in terms of characterization studies of the structures to be obtained and materials that can be used for industry contribute to the literature.

Keywords: Acesulfame, nicotinamide, N,N-diethylnicotinamide, structural characterization, coordination compounds, metal complexes

INTRODUCTION

Acesulfame, potassium acesulfame, a white, odorless, organic and synthetic salt, is a widely used but not metabolizable sweetener in many foods and beverages [1]. In terms of coordination chemistry, acesulfame ligand stands out as a very useful electron donor in the synthesis of inorganic and organometallic molecules [2]. Acesulfame, an oxathiazinone dioxide compound, is systematically named 6-methyl-1,2,3-oxothiazine-4(3H)-one-2,2-dioxide [3]. In addition to its industrial use, acesulfame attracts attention as an interesting ligand in metal complexes with its biological importance and good coordination properties. Discovered by German chemist Karl Clauss in 1967, acesulfame has been studied in fields such as biochemistry, food chemistry, inorganic chemistry, bioinorganic chemistry, analytical chemistry and pharmaceutical chemistry. Its best-known compound is the potassium salt potassium acesulfame (Ace-K) with a similar analogue, 5,6-dimethyl-1,2,3-oxathiazin-4(3H)-one-2,2-dioxide (Figure 1(a)) [4]. It was developed by Karl Clauss and Harald Jensen after the accidental discovery of acesulfame. In the field of inorganic chemistry, the first metal complexes of acesulfame were synthesized in 2005 [5,6]. In the following years, coordination compounds of the acesulfame ligand, especially those containing transition metal cations, were frequently studied [our articles]. Acesulfame is a functional ligand because it has multiple electron-donating groups, such as imine nitrogen, carbonyl oxygen, sulfonyl oxygen, or ring oxygen, on various metal atoms. Although complex structures with transition metal cations are available in the literature [2,3,5,6-12], studies on main group metal cations are quite limited [13-16]. Coordination compounds with earth metals are almost absent. In addition, complexes of some rare earth elements using acesulfame ligand as the electron-donating terminal group have been synthesized and structural studies have been carried out [17-19].

Nicotinamide (or niacinamide) is the amide form of nicotinic acid, or niacin, also known as vitamin B3. Nicotinamide is also called niacinamide, niacin, nicotine acid amide, vitamin PP. Although nicotinamide and nicotinic acid are identical vitamins, their pharmacological effects are very different from each other. Nicotinamide, which has the chemical formula $C_6H_6N_2O$ (Figure 1(b)), has a molecular weight of 122.12 g/mol and a melting point of 128-131°C. The IUPAC name of the compound is 3-pyridine carboxamide. It is a vitamin needed by humans for the production of hydrochloric acid, which is necessary for digestion, as well as for the metabolism of proteins, fats and carbohydrates. While its solubility in water is 100 g/100 ml at 20ºC, its solubility in ethanol is 666 g/100 ml. Moreover, it dissolves very slowly in ether and is insoluble in oils. Nicotinamide is a colorless, crystalline substance with a characteristic odor and taste. Since nicotinamide has a pyridine ring, it gives the same reactions specific to the pyridine ring [20]. It was realized approximately 40 years later that this compound, obtained as a result of the oxidation of nicotine, an alkaloid of tobacco, was a very important vitamin in 1887. The physical and chemical properties of nicotinic acid and nicotinamide, which have the same vitamin value, have been known for a long time [21].

The closed formula of the *N,N*-diethylnicotinamide compound is $C_{10}H_{14}N_2O$ and its molecular weight is 178.12 g/mol. The IUPAC name of the compound is 3-pyridine diethylcarboxamide. This compound, generally called *N,N*-diethylnicotinamide, also has trade names such as cordiamine and nicetamide. Although it has good solubility in water, it is insoluble in oils and ether. Figure 1(c) below shows the structure of *N,N*-diethylnicotinamide. Like nicotinamide, *N,N*-diethylnicotinamide is a colorless, crystalline substance with a unique odor and taste, and gives pyridine reactions due to its pyridine ring. There are many studies in the literature showing that nicotinamide and *N,N*-diethylnicotinamide acts as an electron donor to pyridine nitrogen [22-26]

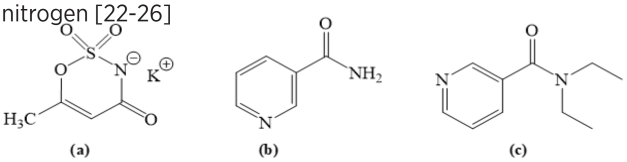


Figure 1. Molecular structures of the ligands of acesulfame anion (a), nicotinamide (b) and N,N-diethylnicotinamide (c).

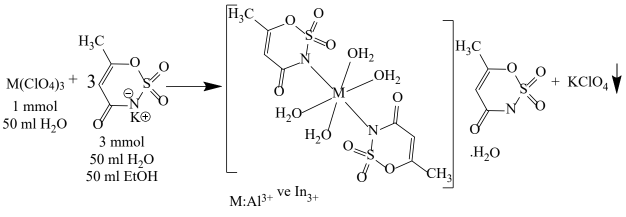
Mixed ligand complexes containing earth metals (Al^{3+} and In^{3+}), which have not been studied in the literature, and acesulfame-nicotinamide or N,N-diethylnicotinamide were synthesized. The structures of the collected complexes were tried to be characterized by FT-IR spectroscopy, elemental analysis, thermal analysis (TG-DTG and DTA) and mass spectroscopy techniques.

MATERYAL METOD

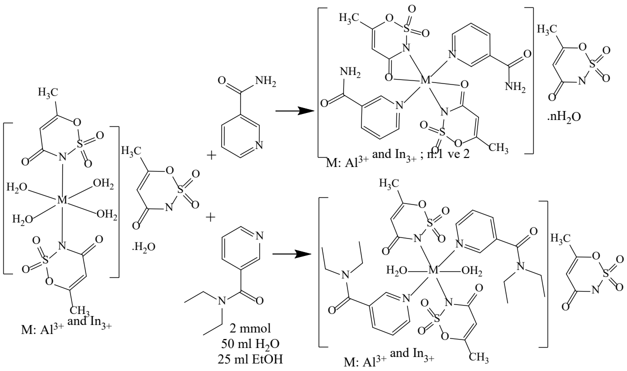
Synthesis

The synthesis reagents, ClO_4^- salts of Al^{3+} and In^{3+} metal cations, potassium acesulfame, nicotinamide and *N,N*-diethylnicotinamide ligands were obtained from Sigma-Aldrich. Pure water and absolute ethanol mixtures (50%:50%) were used as reaction media. For the synthesis, firstly, 1 mmol of potassium acesulfame was dissolved in 50 ml of distilled water in a beaker, and then 3 mmol of Al^{3+} and 3 mmol of In^{3+} were added to perchlorate salt to react. In the reaction, 1:3 (metal:acesulfame) ratio was taken as basis according to charge balance (Scheme 1). With the ethyl alcohol added to the reaction vessel, the potassium perchlorate salt was completely separated from the solution and precipitated. The potassium perchlorate salt precipitate was removed from the total solution by filtration. Care was taken to thoroughly wash the white potassium perchlorate precipitate with distilled water to prevent substance loss. 2 mmol of nicotinamide and *N,N*-diethylnicotinamide ligands solutions formed in ethyl alcohol were added separately to the acesulfame solutions of Al^{3+} and In^{3+} metal cations (Scheme 2).

The resulting final reaction solution was stirred on a magnetic stirrer for approximately 4 hours at 60 ºC. Afterwards, the crystals that precipitated in approximately 3-5 weeks at room temperature with the lid closed were collected by filtration. The crystals were washed with pure water and dried in a vacuum oven at room temperature for analysis.



Scheme 1. Synthesis reaction of Al^{3+} and In^{3+} metal cations salts of acesulfame ligand.



Scheme 2. Synthesis reaction of Al^{3+} and In^{3+} metal cation center complexes containing acesulfame and nicotinamide / *N,N*-diethylnicotinamide ligands.

Elemental Analysis

Elemental analysis results of metal-acesulfame-nicotinamide / *N,N*-diethylnicotinamide mixed ligand coordination compounds using Al^{3+} and In^{3+} earth metal cations as electron acceptors are summarized in Table 1. The colors of the complex molecules were determined as pale/off-white, as expected, depending on the electronic configurations of the central atoms in the 3+ oxidation state. Since the *"d"* orbitals of metal cations are filled, electronic transitions that cause color formation are prohibited. For this reason, color formation is not observed. However, slight impurity colors can be detected due to electronic transitions caused by charge transfer from the ligand to the metal. The agreement of experimental and theoretical results obtained from elemental analysis supports the molecule formulations proposed by us.

Infrared (FT-IR) Spectroscopy Studies

According to the FTIR spectra (Figure 2) recorded in the range of 4000 cm⁻¹ – 400 cm⁻¹, it was found that -OH stretching bands originating from H_2O molecules appeared in the regions of approximately 3650 cm⁻¹-2850 cm⁻¹ in all structures. While N-H stretches originating from nicotinamide were detected in the 3521 cm⁻¹ and 3517 cm⁻¹ bands in structures only I and II, the absence of any stretch peak belonging to this group in structures III and IV is evidence of the ionized coordination of the acidic N-H group in the ring of acesulfame ligands in all structures. The bending peaks of the N-H bonding of the amide group were also observed at 1586 cm⁻¹ and 1588 cm⁻¹

Table 1. Chemical composition data of for mixed-ligand metal-acesulfame-nicotinamide and *N,N*-diethylnicotinamide complexes

Complex	M.A. (g/mol)	Yield	Content (%) exp. (theo.)				Colour	Decomp Temp. (°C)
			C	H	N	S		
$[Al(C_6H_6N_2O)_2\ (C_4H_4NO_4S)_2](C_4H_4NO_4S).2H_2O$ $C_{24}H_{28}AlN_7O_{16}S_3$ **(I)**	793.68	85	36.12 (36.32)	3.87 (3.56)	12.21 (12.35)	12.39 (12.12)	White	77
$[In(C_6H_6N_2O)_2\ (C_4H_4NO_4S)_2](C_4H_4NO_4S).H_2O$ $C_{24}H_{26}InN_7O_{15}S_3$ **(II)**	863.50	83	33.07 (33.38)	3.67 (3.03)	11.55 (11.35)	11.41 (11.14)	pale-white	88
$[Al(C_{10}H_{14}N_2O)_2(C_4H_4NO_4S)_2\ (H_2O)_2](C_4H_4NO_4S)$ $C_{32}H_{44}AlN_7O_{16}S_3$ **(III)**	905.90	72	42.88 (42.43)	4.67 (4.90)	10.96 (10.82)	10.87 (10.62)	White	135
$[In(C_{10}H_{14}N_2O)_2(C_4H_4NO_4S)_2(H_2O)_2](C_4H_4NO_4S)$ $C_{32}H_{44}InN_7O_{16}S_3$ **(IV)**	993.74	70	39.75 (38.68)	4.63 (4.46)	9.98 (9.87)	9.47 (9.68)	pale-white	141

for complexes I and II, respectively. The presence of ν(C-N-C)$_{ace}$ stretching peaks for acesulfame and pyridinic ν(C-N-C)$_{pyrd}$ group observed in all structures support the existence of ligands in coordination compounds as in the proposed structural formulas. The fact that the numerical difference between the symmetric and asymmetric stretching vibrations of the -SO_2 groups is compatible with the difference in the potassium salt of acesulfame is evidence that coordination does not occur through this group. The most important evidence of the molecular formulations we propose is the presence of binding peaks in which the ligands coordinate with metal cations. Accordingly, ν(M-N)$_{ace}$ stresses are 649 cm^{-1}-620 cm^{-1}, ν(M-N)$_{pyrd}$ stresses are 673 cm^{-1}-648 cm^{-1}, ν(M-O)$_{ace}$ stresses (only in structures I and II) 507 cm^{-1}-509 cm^{-1} and finally ν(M-O)$_{aqua}$ stresses (only in structures III and IV) were detected in the 545 cm^{-1}- 543 cm^{-1} regions, respectively. Data on binding peaks showing the characteristic binding properties of all structures are summarized in Table 2.

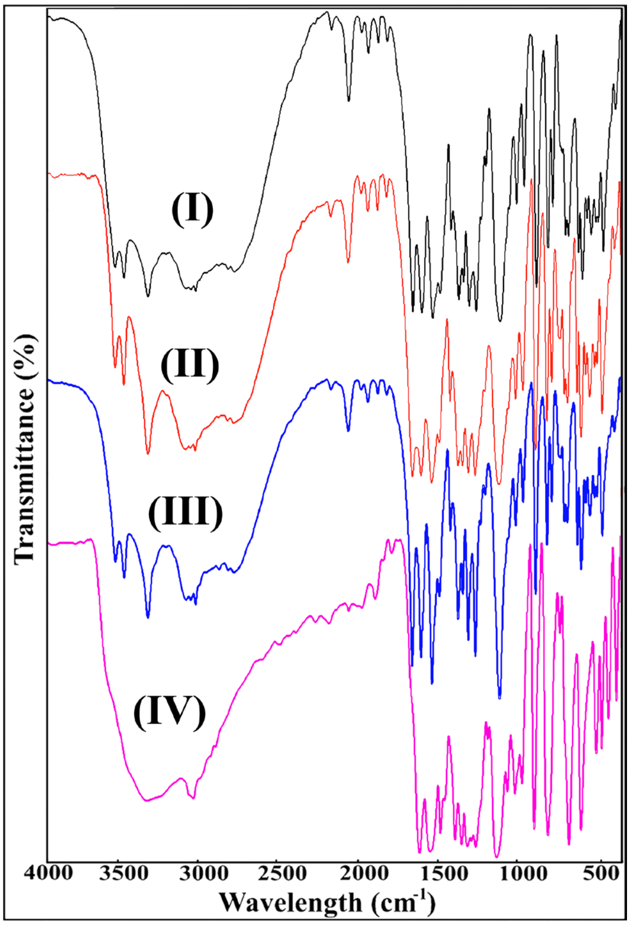


Figure 2. FTIR spectra of mixed-ligand metal-acesulfame-nicotinamide and *N,N*-diethylnicotinamide complexes

Table 2. Important infrared peak data for mixed-ligand metal-acesulfame-nicotinamide and *N,N*-diethylnicotinamide complexes

Groups	(I)	(II)	(III)	(IV)
$\nu(OH)_{H2O}$	3650-2850	3650-3150	3550-3150	3600-3050
ν_{ger}(N-H)	3521	3517	-	-
ν(=C-H)	3372	3370	3406	3401
ν(C=O)$_{ace}$	1655	1654	1652	1650
$\nu_{eğ}$(N-H)	1586	1588	-	-
ν(C=C)	1540	1540	1554	1549
ν(C-N-C)$_{ace}$	1357	1357	1363	1364
ν(C-N-C)$_{pyrd}$	1393	1393	1394	1394
$\nu_{as}(SO_2)$/ $\nu_s(SO_2)$	1314/1162	1314/1165	1319/1173	1321/1175
ν_{as-s}	152	149	146	146
ν(ring)	1061-834	1060-833	1090-840	1093-842
ν_s(CNS)/ ν_{as}(CNS)$_{ace}$	1323/935	1321/934	1309/938	1310/938
ν(C-N)	1013-735	1014-734	1014-723	1016-721
ν(M-N)$_{ace}$	649	649	620	621
ν(M-N)$_{pyrd}$	673	673	645	648
ν(M-O)$_{aqua}$	-	-	545	543
ν(M-O)$_{ace}$	507	509	-	-

Thermal Analysis Studies

Thermal analysis curves recorded in an inert nitrogen atmosphere in the temperature range of 25-1000 ºC are shown in Figure 3. The synthesized four different mixed ligand coordination compounds were classified as nicotinamide and N,N-diethylnicotinamide (III and IV) according to their secondary ligands. While the degradation characteristics of Al^{3+} (I) and In^{3+} (II) complexes containing nicotinamide are similar to each other, it has been determined that the degradation characteristics of Al^{3+} (III) and In^{3+} (IV) complexes containing N,N-diethylnicotinamide ligand are also similar. The decomposition of complexes I and II begins with the dehydration of the hydrate waters present in the structures. In complex I containing two hydrated waters, primary decomposition occurs with an experimental weight loss of 4.80% (theoretically 4.54%) in the temperature range of 48-101 ºC. In Structure II, the removal of hydrated water with a weight loss of 2.29% experimentally (2.09% theoretically) occurred in the temperature range of 68-140 ºC. In the secondary degradation step, the organic ligands for both structures begin to decompose. While the SO_2 groups of the three acesulfame ligands present in complex II are separated (142-241 ºC), the nicotinamide ligands in structure I are degraded. For structure I, the removal of SO_2 groups took place in the temperature region of 290-386 ºC. For structure I, the degradation of organic derivatives occurs via nicotinamide, while for structure II, this occurs via acesulfame ligands. The internal compatibility of the experimental and theoretical weight losses of the organic derivatives proposed for the degradation steps of organic ligands for both complexes supports the proposed degradation products (Table 3). While complex I completes its decomposition in six steps, structure II transforms into its oxide in five steps. The decompositions of coordination compounds with N,N-diethylnicotinamide ligands (III and IV) are characteristically more similar to each other. While both complexes decompose in four steps, the first step indicates the removal of two ligand water and one SO_2 group each located in the coordination spheres. In complexes that become dehydrated, it is recommended to separate one SO_2 group as a secondary step. The third degradation step of both structures is interpreted as the step in which the acesulfame ligands are completely disintegrated and removed from the reaction environment, and the consistency of experimental and theoretical weight losses supports this claim (Table 3). The last degradation steps of the structures were attributed to the degradation of N,N-diethylnicotinamide ligands. The proposed final decomposition products of all complexes were thought to be oxides of the relevant metal cations, and the experimental and theoretical weight losses found also support the existence of metal oxides. It has been determined that the experimental weight losses of the final residue products are approximately 1% higher than the theoretical weight losses. The reason for this has been shown to be that during thermal decomposition in an inert nitrogen atmosphere, complete combustion does not occur due to the lack of sufficient oxygen in the environment, and some carbonized coal residue accumulates on the surface of the metal oxides. The fact that metal oxides, which are expected to be white in color, are collected in black color is also evidence supporting our suggestion. Detailed degradation properties of all complexes are summarized in Table 3.

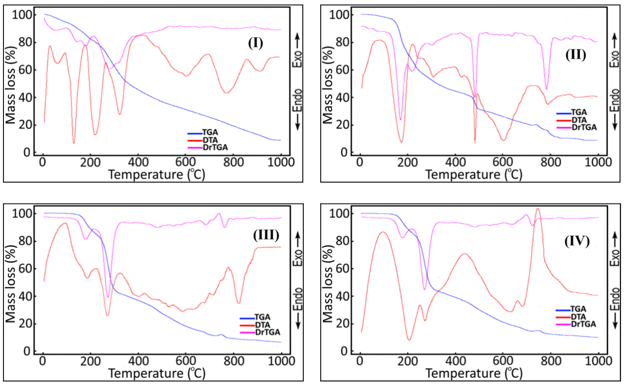


Figure 3. Thermal decomposition curves (TG/DTA) of Al^{3+} and In^{3+} mixed ligand complexes with acesulfama-nicotinamide and *N,N*-diethylnicotinamide.

Table 3. Thermal analysis data of Al^{3+} and In^{3+} mixed ligand complexes with acesulfama-nicotinamide and *N,N*-diethylnicotinamide.

Compounds		Temp. range (˚C)	DTA_{max} (˚C)	Removing group	Mass Loss (%)		Remaining Product (%)		Decomp. Product	Colour
					Exp.	Theo.	Exp.	Theo.		
$[Al(C_6H_6N_2O)_2(C_4H_4NO_4S)_2](C_4H_4NO_4S).2H_2O$										white
$C_{24}H_{28}AlN_7O_{16}S_3$	1	48-101	79	$2H_2O$	4.80	4.54				
793,69 g/mol	2	102-193	147	$2CH_2NO$	10.97	11.09				
	3	194-288	235	$2C_5H_5N$	19.12	19.65				
	4	290-386	336	$3SO_2$	24.62	24.22				
	5	388-940	611;771;916	$3C_4H_4NO;3/2O$	33.77	34.18	5.79	6.43	$1/2Al_2O_3$	black
$[In(C_6H_6N_2O)_2(C_4H_4NO_4S)_2](C_4H_4NO_4S).H_2O$										pale-white
$C_{24}H_{26}InN_7O_{15}S_3$	1	68-140	130	H_2O	2.29	2.09				
863,51 g/mol	2	142-201	183	$3SO_2$	22.62	22.26				
	3	202-343	221; 295	$2C_6H_6N_2O$	28.24	28.29				
	4	344-481	430	3CO	9.86	9.73				
	5	482-512	491	C_2H_3	8.95	9.38				
	6	513-931	607;739;871	CHN;3/2O	11.77	12.27	15.12	16.08	1/2In2O3	black
$[Al(C_{10}H_{14}N_2O)_2(C_4H_4NO_4S)_2(H_2O)_2](C_4H_4NO_4S)$										white
$C_{32}H_{44}AlN_7O_{16}S_3$	1	103-198	190	$2H_2O;SO_2$	10.82	11.05				
905,90 g/mol	2	200-231	218	SO_2	6.52	7.07				
	3	232-306	285	$3C_4H_4NO_2;SO_2$	38.92	39.55				
	4	308-903	401;512;596;810	$2C_{10}H_{14}N_2;$ $2C_{10}H_{14}N_2O_{1/2}$	36.89	36.69	6.85	5.63	$1/2Al_2O_3$	black
$[In(C_{10}H_{14}N_2O)_2(C_4H_4NO_4S)_2(H_2O)_2](C_4H_4NO_4S)$										pale-white
$C_{32}H_{44}InN_7O_{16}S_3$	1	110-196	185	$2H_2O;SO_2$	9.81	10.07				
993,74 g/mol	2	198-241	214	SO_2	6.78	6.45				
	3	242-302	281	$3C_4H_4NO_2;SO_2$	37.05	36.06				
	4	305-897	-426;615;680;-731	$C_{10}H_{14}N_2$; $C_{10}H_{14}N_2O_{1/2}$	31.51	33.35	14.85	13.97	$1/2In_2O_3$	black

Ultraviolet-Visible Spectroscopy Studies

The UV-Vis spectra recorded in the 200-900 nm range of the structures of the mixed ligand complexes containing synthesized metal-acesulfame-nicotinamide / *N,N*-diethylnicotinamide are as follows. When the recorded solid-state UV-VIS spectroscopic curves of metal ions with group IIIA 3+ cationic charge valence were examined, no significant peak was observed in the 750-400 nm range, which corresponds to the band transition regions of the metals. Since the "*d*" orbitals of earth elements, which undergo splitting under UV light in the 3+ cationic oxidation state, do not undergo any splitting, the "*d-d*" transitions seen in transition metals are not observed. The most obvious result of this effect is the colors of the synthesized complexes, and the color of all complexes is either colorless or close to pale white. When the spectra of all metal complexes are examined, it is assumed that the high intensity but numerically evaluable peaks (M-L) occurring in the 300-200 nm region may belong to electron transitions from the metal to the ligands.

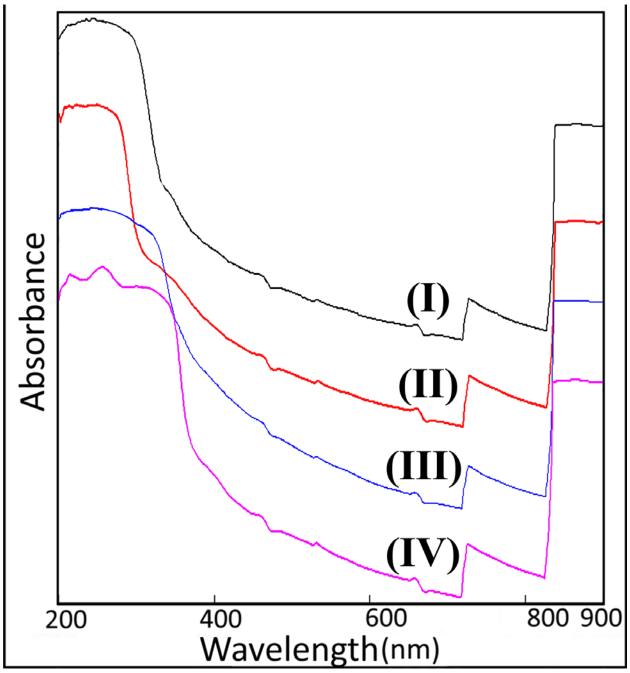


Figure 4. Solid State UV-Vis spectra of Al^{3+} and In^{3+} mixed ligand complexes with acesulfama-nicotinamide and *N,N*-diethylnicotinamide.

Mass Spectroscopy (GC-MS) Studies

When the thermal analysis curves of metal-acesulfame-nicotinamide and metal-acesulfame-N,N-diethylnicotinamide mixed ligand complexes are examined, it is seen that the degradation of the complexes is similar. Decomposition begins with deaquatation and continues with the formation of SO_2 by acesulfamate ligands. Similar results are seen when the mass spectra of these complexes are examined. There are also peaks resulting from the removal of nicotinamide and N,N-diethylnicotinamide ligands from mixed ligand complexes. Although multiphase distortions are generally observed in the mass spectra, the most prominent peaks in the spectra have been tried to be explained. The mass spectra of complexes I and II are given in Figures 5 and 6. Peaks whose m/z ratio corresponds to the removal of acesulfamate ions are seen at 161.22 and 161.02 m/z, respectively. The peaks corresponding to the removal of nicotinamide ions were detected at m/z 121.01- 121.20, respectively. Formulations that can be attributed to possible degradation products of the breakdown of the complexes, taking into account the molecular ion peaks, are shown in Figures 7 and 8.

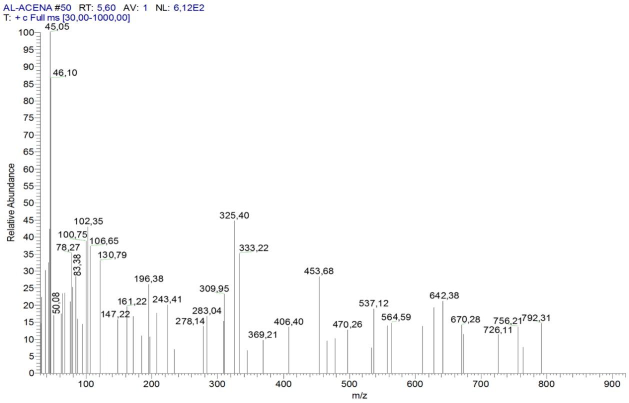


Figure 5. Mass spectrum pattern of complex I.

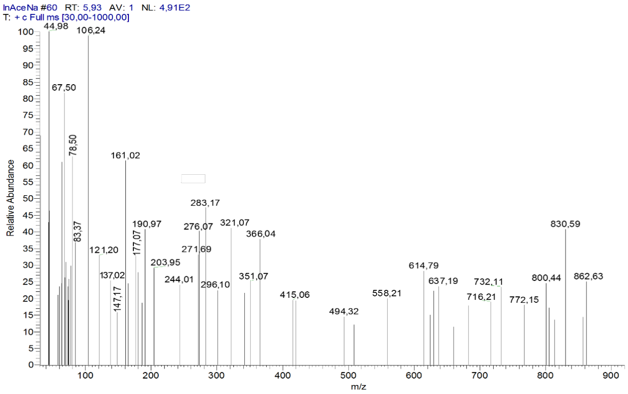


Figure 6. Mass spectrum pattern of complex II.

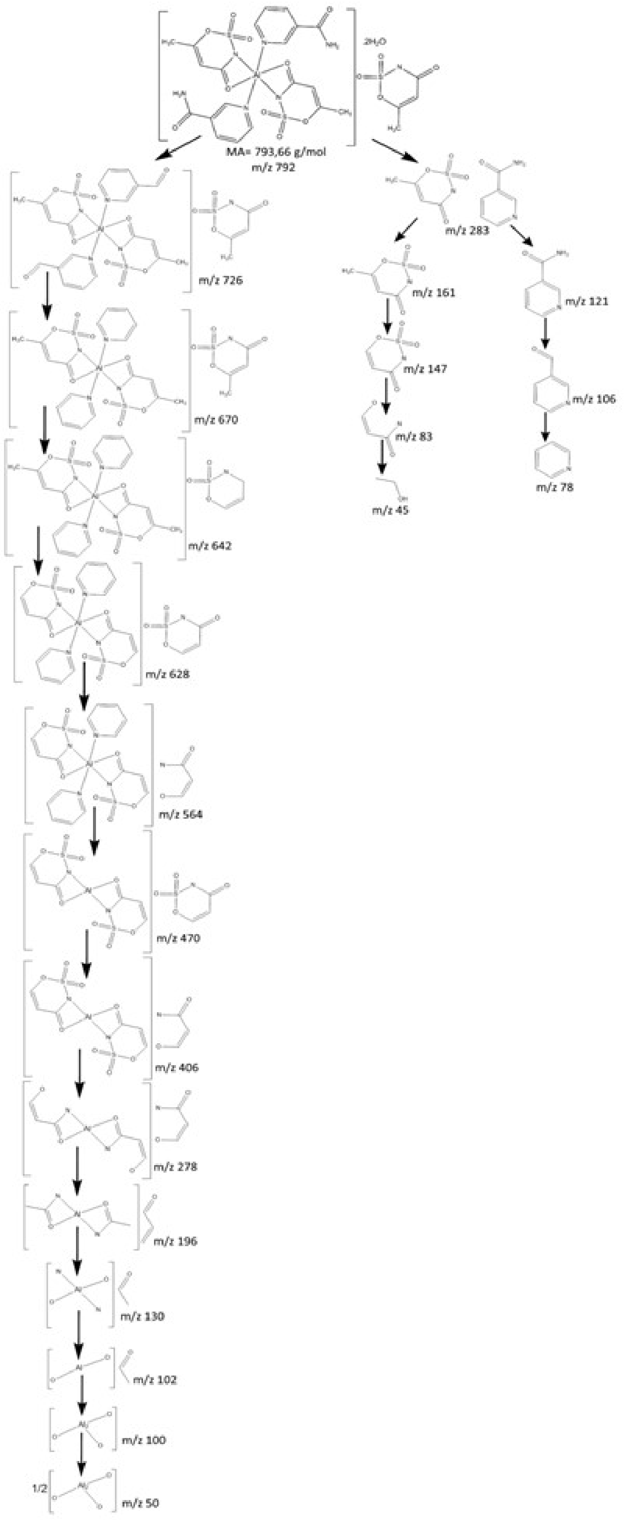


Figure 7. Possible molecular ion formulations and degradation schematics of the degradation products of complex I.

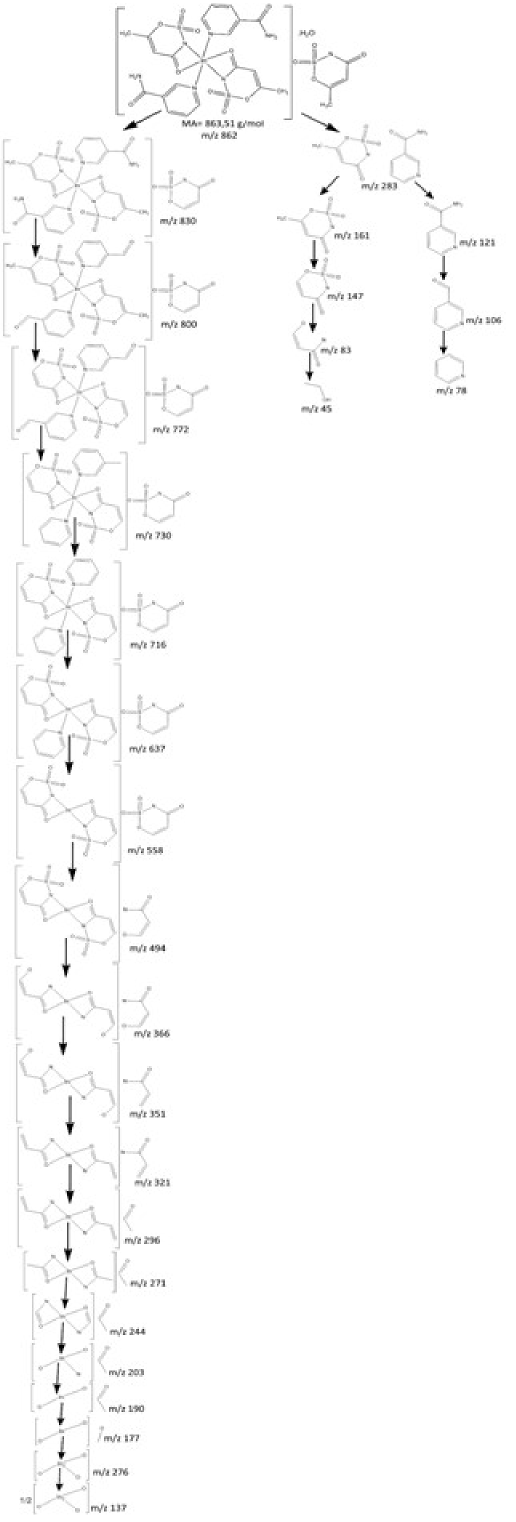


Figure 8. Possible molecular ion formulations and degradation schematics of the degradation products of complex II.

Figures 9 and 10 show the mass spectra of complexes III and IV, respectively. Peaks whose m/z ratio corresponds to the removal of acesulfamate ions are seen at 161.22 and 161.12 m/z, respectively. The peaks corresponding to the removal of N,N-diethylnicotinamide ions appeared at 177.24 and 177.17 m/z, respectively. Formulations that can be attributed to possible degradation products of the breakdown of the complexes, taking into account the molecular ion peaks, are also shown in Figures 11 and 12.

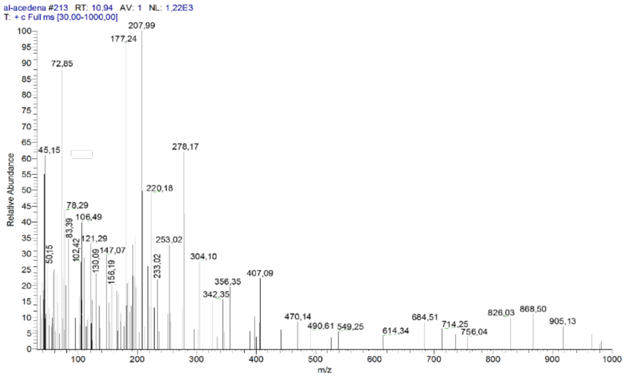


Figure 9. Mass spectrum pattern of complex III.

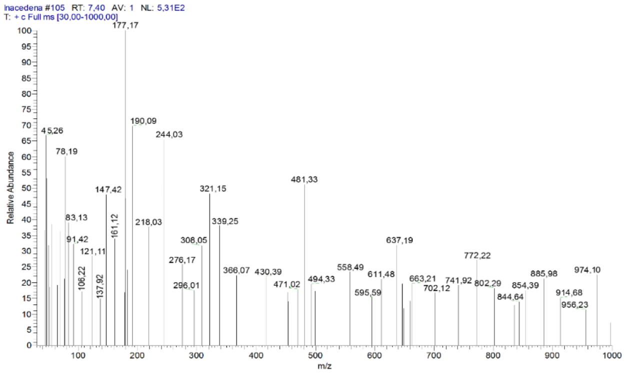


Figure 10. Mass spectrum pattern of complex IV.

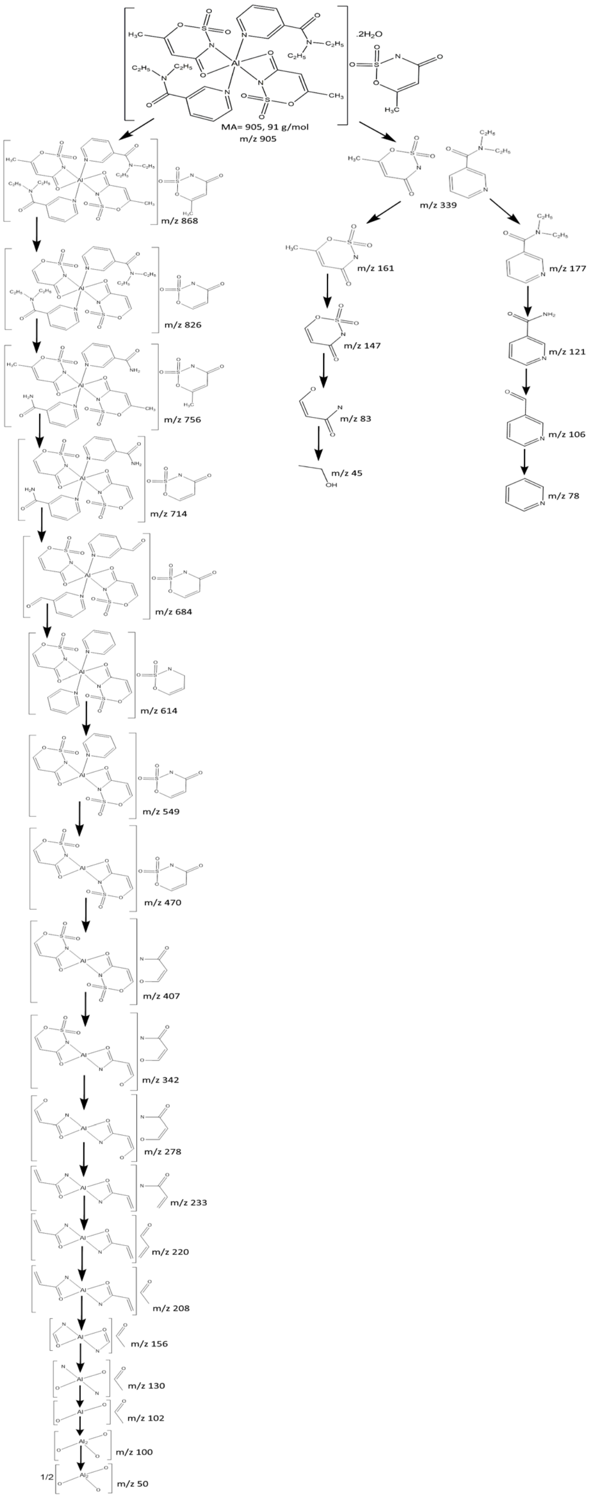


Figure 11. Possible molecular ion formulations and degradation patterns of the degradation products of the complex III.

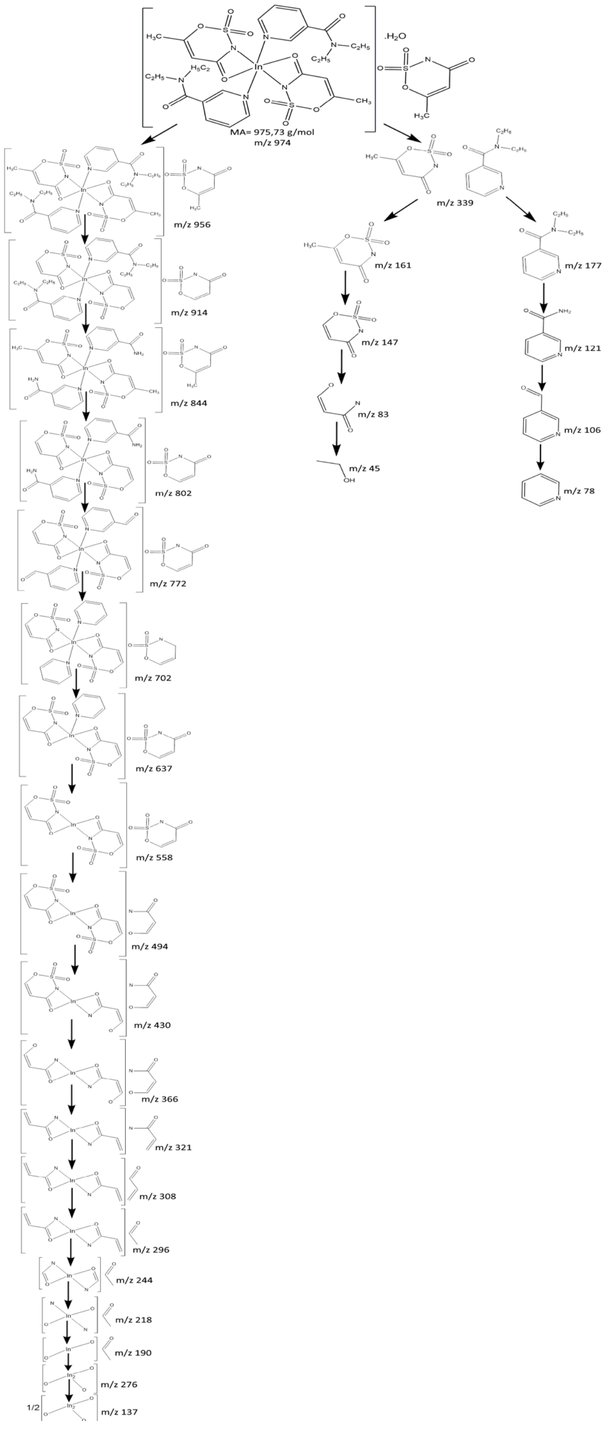


Figure 12. Possible molecular ion formulations and degradation pattern of the degradation products of the complex IV.

CONCLUSIONS

In this thesis, new complexes of group 3A Al^{3+} and In^{3+} metals with acesulfame-nicotinamide and acesulfame-N,N-diethylnicotinamide mixed ligands were synthesized for the first time. The structures of these synthesized complexes were elucidated by elemental analysis, infrared spectroscopy, thermogravimetric analysis, solid ultraviolet-visible region spectroscopy, mass analysis and melting point determination methods. According to the results of the elemental analysis of the complexes, it was determined that the metal:ligand1:ligand2 ratios in mixed ligand complexes were 1:3:2. While hydrate waters are located outside the coordination sphere in complexes I and II, it has been suggested that there may be two ligand waters each inside the coordination sphere in structures III and IV. In all structures, it is predicted that two monoanionically acesulfame ligands are involved in coordination, while one of each is located outside the coordination sphere to ensure charge balance. For this reason, we can say that all complexes are cationic salt-like structures. It has been claimed that the coordination of metal cations is six and the geometries of the structures may also be decomposed octahedral. It was determined by infrared analysis that the neutral ligands nicotinamide and N,N-diethylnicotinamide molecules bind to the metal cation through the nitrogen atom of pyridine. While it has been suggested that acesulfame ligands provide monoanionic-bidentate coordination in complexes I and II, acesulfame ligand is in monoanionic-monodentate coordination in structures III and IV. Proposed explicit structural formulas for metal-acesulfame-nicotinamide and metal-acesulfame-N,N-diethylnicotinamide mixed ligand complexes are shown in Figure 13(a) and (b).

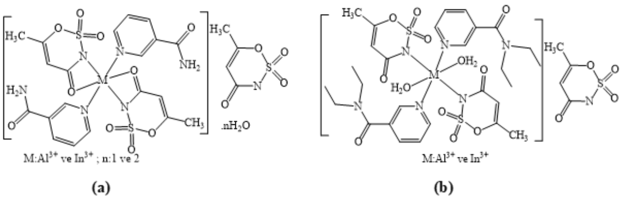


Figure 13. Molecular structure formulations of acesulfame-nicotinamide and *N,N*-diethylnicotinamide mixed ligand complexes of Al^{3+} and In^{3+} metal cations.

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