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Mixed Ligand Complexes of Acesulfame/Nicotinamide with Earth Alkaline Metal Cations Mg^{II}, Ca^{II}, Ba^{II} and Sr^{II}. Synthesis and Characterization

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ABSTRACT

In the scope of this study, acesulfame (ace, acs)-nicotinamide (na) mixed ligand complexes of Mg(II), Ca(II), Sr(II) and Ba(II) were synthesized for the first time. Possible formulas for complexes were determined as $[Mg(H_2O)_4(na)_2](acs)_2$, $[Ca(H_2O)_6(na)_2](acs)_2$, $[Sr(H_2O)_7(na)_2](acs)_2$, $[Ba(H_2O)_7(na)_2](acs)_2$). It was observed that acesulfame ligands within structure were located two moles each at outer surface of coordination sphere acting as counter-ion allowing the charge balance of structure. The solubility of compounds gaining ionic character in this way was determined as quite well as compared to complex structures. Characterizations of complexes synthesized were performed via melting point analysis, elemental analysis, mass spectroscopy and FT-IR spectroscopy methods. Thermal properties of complexes obtained were determined with tandem TG-DTG and DTA techniques. It was found that the coordination spheres of metal cations within compounds obtained in this study were filled with nicotinamide and aqua ligands.

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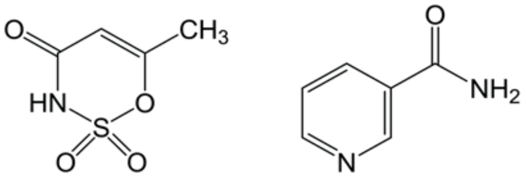
Key words:
Acesulfame; Nicotinamide; Earth Alkaline Metals; Coordination Compound; Thermal Properties.

INTRODUCTION

The compound (Figure 1) with the trade name of acesulfame ($C_4H_4KNO_4S$, 201.242 g / mol), and with the nomenclature such as 6-methyl-1,2,3-oksotiaz-4 (3H) -on-2,2-dioxide, 6-methyl-2,2-dioksooksotiaz-4-on (IUPAC) is oxatiazinon dioxide. Moreover, it is also known as 6-methyl-3,4-dihydro-1,2,3-oksotiaz-4-on 2,2-dioxide, 1,2,3-oksotiazin-4(3H)-on-6-methyl-2,2-dioxide [1]. There are nitrogen and oxygen (in the ring); sulphonyl, methyl and carbonyl groups within the acesulfame structure. Because hydrogen atom bounded to nitrogen is quite acidic (pKa: ~ 2), it easily forms potassium salt. Today, use of acesulfame as a sweetener in beverages and food products is permitted. Potassium acesulfame is not metabolized in the body and does not produce energy. Acesulfame solution of 3% is 200 times sweeter than table sugar (sucrose) [2].

Nicotinamide is the compound with the chemical formula of $C_6H_6N_2O$ (Figure 1), molecular weight of 122.12 g/mol and the IUPAC name of 3-pyridine carboxamide. Basically, being an amide derivative of nicotinic acid, nicotinamide is also called as niacinamide, niacin, nicotinic acid amide, Vitamin PP and Vitamin B3. Nicotinamide with a peculiar smell and taste is a colourless crystalline substance. Because nicotinamide has pyridine ring, it gives characteristic pyridine reactions [3-7].

First metal complexes of acesulfame have been reported at 2005 [8,9]. Bis (acesulfamato-κ^2N^3,O^4) bis (2-aminopyirimidine-κN^1) copper (II) acesulfame is the



(a) (b)

Figure 1. a) Acesulfame, **b)** Nicotinamide

first mixed ligand complex in the literature. The structure analysis of the complex was performed using X-Ray method and it was determined that acesulfame ligands are located at trans position and behave as bidentate ligand through nitrogen of imine and oxygen of carbonyl. It was also observed that 2-aminopyrimidine, secondary ligand, in the complex is almost planar.

It was detected that the molecular geometry of the complex is distorted octahedral due to Jahn-Teller effect and the effect of four membered chelate ring. The other conclusion obtained from experimental data is the hydrogen bonding between carbonyl oxygen of acesulfamato and 2-aminopirimidine ligand. Bis(acesulfamato-κ^2N^3, O^4) bis(2-aminopyrimidine-κN^1) copper (II) complex having four membered chelating ligand has the octahedral geometry [8]. The ring nitrogen of the acesulfamate ligand is more extended and in the axial position. Acesulfamate ligand within the structure at trans position acts as bidentate ligand via binding to Cu(II) ion through nitrogen of the ring and carbonyl oxygen. Octahedral geometry was achieved by the two neutral 2-aminopyrimidine ligand behaving as monodentate ligand. $[Ni\ (dmen)_2(H_2O)_2](acs)_2$ complex was the first complex within which acesulfamate anion acts as charge balancer [10]. At a comprehensive study performed for acesulfame metal complexes, details about synthesis, structure and properties of complexes with the general formula of $[M(acs)_2(H_2O)_4]$(M:Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, $[M(acs)_2(H_2O)_2]$(M: Zn^{2+} and Cd^{2+}) were investigated [11]. Crystalline structure of $[Co(acs)_2(H_2O)_4]$, one of the complexes synthesized, was investigated and it was determined that acesulfamato ligand is coordinated to Co(II) ion at trans position through imine nitrogen. For $[Co(acs)_2(H_2O)_4]$ complex, it was observed that there is intermolecular interaction (hydrogen bonding) between sulphonyl oxygen atoms of acesulfamato ligand and hydrogen atoms of aqua ligands and also both intermolecular and intramolecular interaction (hydrogen bonding) between carbonyl oxygen atoms of acesulfamato and hydrogen atoms of aqua ligands. Some complex structures stated have thermochromic, solvatochromic and ionochromic properties depending on deaquation [12]. Also, the alkaline earth metal cation complexes with organic ligands were studied and investigated their bonding parameters by lots of researcher [13-18]

The importance of studies related with transition metal complexes of nicotinamide acting as vitamin B_3 and used in drug preparation has been increased recently. As a result of spectral investigation of complexes between nicotinamide and these metals, it was determined that it has ability to bind as monodentate ligand through pyridine nitrogen. [19-21].

MATERIALS AND METHODS

In the synthesis of complex, $Ca(ClO_4)_2.4H_2O$ and $Sr(ClO_4)_2$ were obtained from Aldrich, $Mg(ClO_4)_2.2H_2O$ and $Ba(ClO_4)_2$ were obtained from Merck, potassium acesulfame (Kacs, Kace), and nicotinamide were obtained from Fluka, and ethanol was obtained from Aldrich. Pure water was used as a solvent.

For the synthesis of complex, metal perchlorate and potassium acesulfame were used sufficient amount at molar ratio of 1:2 (typically molar ratio of 0.01: 0.02) and dissolved within separate beaker. Resulting solutions were stirred slowly and, as shown in the following reaction, precipitation of $KClO_4$ salt and the formation of complexes were provided.

$$M(ClO_4)_2 + 2\ K(acs) \rightarrow 2\ KClO_4 + [M(acs)_n(H_2O)_x]$$

The mixed ligand complexes were obtained after synthesis of $[M(acs)_n(H_2O)_x]$ complex via mixing of both aqueous solutions of each component (metal, nicotinamide) with metal/nicotinamide ratio of 1:2.

$$[M(acs)_n(H_2O)_x] + 2\ \text{nicotinamide} \rightarrow [M(acs)_n(H_2O)_y(na)_m]$$

8 complexes having the following formula were synthesized by these methods:

$[Mg(H_2O)_4(na)_2](acs)_2$, $[Ca(H_2O)_6(na)_2](acs)_2$,
$C_8H_{10}SrN_2O_9S_2$, $Ba(H_2O)_7(na)_2](acs)_2$

Resulting complexes were characterized by analytical

Table 1. Data obtained from elemental analysis of complexes

Compounds	Molecular Weight (g/mol)	%C Experimental (Theoretical)	%H Experimental (Theoretical)	%N Experimental (Theoretical)
$[Mg(H_2O)_4(na)_2](acs)_2$	664,83	35,84(36,13)	5,67(4,25)	12,69(12,64)
$[Ca(H_2O)_6(na)_2](acs)_2$	717,31	33,16(33,49)	4,99(4,5)	10,91(11,72)
$[Sr(H_2O)_7(na)_2](acs)_2$	782,15	31,24(30,7)	4,21(4,4)	9,66(10,75)
$[Ba(H_2O)_7(na)_2](acs)_2$	831,87	27,65(28,88)	4,11(4,12)	8,67(10,1)

methods such as IR spectroscopy, X-ray single crystal diffraction, thermal analysis, melting point determination, mass spectroscopy and elemental analysis methods.

RESULTS AND DISCUSSION

Elemental analysis results obtained for metal-aqua-nicotinamide-acesulfame salt-type mixed ligand complexes are given by Table 1. Being in harmony with the calculated values of the experimental results obtained by elemental analysis supports the validity of the proposed formula.

Melting points of complexes were determined by heating at the temperature interval of 20-300°C with 5°C/min heating rate using Stuart SMP30 device. As can be seen from Table 2, potassium acesulfame melts at 225°C, whereas it was observed that salt-type complex structure decomposes accompanied by darkening without melting.

Table 2. Melting points of potassium acesulfame and complexes

Compound	Temp. (°C)	Observations
Potassium Acesulfame	225	Melting
$[Mg(H_2O)_4(na)_2](acs)_2$	121-132	Darkening/Decomposition
$[Ca(H_2O)_6(na)_2](acs)_2$	210-235	Darkening /Decomposition
$[Sr(H_2O)_7(na)_2](acs)_2$	257-269	Darkening /Decomposition
$[Ba(H_2O)_7(na)_2](acs)_2$	206-250	Darkening /Decomposition

Infrared Spectra

As can be seen from FT-IR spectra given by Figure 2 for salt-type complex compounds synthesized, there are O-H stretching vibrations at 3565 and 3431 cm^{-1} for the compound $[Mg(H_2O)_4(na)_2](acs)_2$. There are stretching vibrations observed at 3369 and 3303 cm^{-1} for N-H, at 3211 cm^{-1} for aromatic C-H and at 3075 cm^{-1} for aliphatic C-H. Vibrations for carbonyl (C=O) groups were observed at $1688_{(amide)}$ and $1651_{(acs)}$ cm^{-1}. N-H group bending and C=C stretching vibrations were observed at 1599 and 1550 cm^{-1}, respectively. Asymmetric and symmetric stretching vibrations for sulphonyl group were observed at 1311 and 1169 cm^{-1}, respectively. Asymmetric and symmetric stretching vibrations for C-N-S were observed at 939 and 1396 cm^{-1}, respectively. Metal-oxygen and metal-nitrogen bonds were observed in order of at 517 and 560 cm^{-1}.

Sharp bands observed at 3518 and 3423 cm^{-1} for $[Ca(H_2O)_6(na)_2](acs)_2$ complex are belongs to O-H stretching vibrations. Stretching vibrations for N-H (NH_2 group) can be seen at 3368 and 3296 cm^{-1}. Aromatic and aliphatic C-H stretching vibrations can be observed at 3060 and 2960 cm^{-1}, respectively. Another data obtained from spectra are stretching vibration of the carbonyl group at $1678_{(amide)}$ and $1650_{(acs)}$ cm^{-1}, N-H bending vibrations at 1600 cm^{-1}, C=C vibrations at 1578 cm^{-1}. Moreover, asymmetric and symmetric stretching vibrations for sulphonyl and C-N-S groups are observed at 1270 and 1176 cm^{-1}, and at 936 and 1385 cm^{-1}, respectively.

It was determined that $[Sr(H_2O)_7(na)_2](acs)_2$ complex also gives sharp O-H stretching vibration bands at 3577 and 3520 cm^{-1}. The bands observed at 3370 and 3290 cm^{-1} correspond to N-H stretching vibration. Aromatic and aliphatic C-H stretching vibrations are observed at 3143-3070 and 2824 cm^{-1}, respectively. Sharp bands observed at $1706_{(amide)}$, 1675 and $1656_{(acs)}$ are belongs to carbonyl

Table 4.2. Characteristic FT-IR vibration values (cm^{-1}) for Acesulfame/Nicotinamide-Metal complexes (cm^{-1}).

Compound	ν(OH)	$ν_{ger}$(NH)	ν(C-H)	ν(C=O)	$ν_{eg}$(NH)	ν(C=C)	$ν_{as}(SO_2)$	$ν_s(SO_2)$	$ν_s$(CNS)	$ν_{as}$(CNS)	M-O/M-N
$[Mg(H_2O)_4(na)_2](acs)_2$	3565 3431	3369 3303	3211 3075	1688 1651	1599	1550	1311	1169	1396	939	517/560
$[Ca(H_2O)_6(na)_2](acs)_2$	3518 3423	3368 3296	3060 2960	1678 1650	1600	1579	1270	1176	1385	936	520/557
$[Sr(H_2O)_7(na)_2](acs)_2$	3577 3520	3370 3300	3142 2824	1675 1656	1610	1588	1251	1160	1358	936	518/570
$[Ba(H_2O)_7(na)_2](acs)_2$	3592 3527	3367	3110 2923	1676 1652	1600	1558	1320	1176	1368	941	523/563

(C=O) group stretching vibrations. Bending vibration of NH_2 group and C=C double bond stretching vibration are observed at 1610 and 1588 cm^{-1}, respectively. Asymmetric and symmetric stretching vibrations for sulphonyl (SO_2) and C-N-S group are observed at 1251 and 1160 cm^{-1}, and 936 and 1358 cm^{-1}, respectively.

According to the FT-IR spectra analyzed for $[Ba(H_2O)_7(na)_2](acs)_2$, sharp bands observed at 3592 and 3527 cm^{-1} may be attributed to O-H stretching vibration. While one of the bands due to N-H stretching belongs to NH_2 can be observed at 3367 cm^{-1}, other band could not be seen due to the expansion of the aromatic C-H band. C-H stretching vibrations can be observed at 3161-3110 (aromatic) and 2923 (aliphatic) cm^{-1}. Stretching vibration of Carbonyl (C = O) group can be seen at $1676_{(amide)}$ and $1652_{(acs)}$ cm^{-1}. There are other vibrations observed for N-H bending at 1600 cm^{-1}, for C=C double bond stretching at 1558 cm^{-1}, asymmetric and symmetric stretching for sulphonyl group at 1320 and 1176 cm^{-1}. Asymmetric and symmetric stretching vibration bands for C-N-S groups were observed at 941 and 1368 cm^{-1}, respectively.

Thermal Analysis

Figure 3a shows thermal analysis curves for $[Mg(H_2O)_4(na)_2](acs)_2$ complex. The complex having four

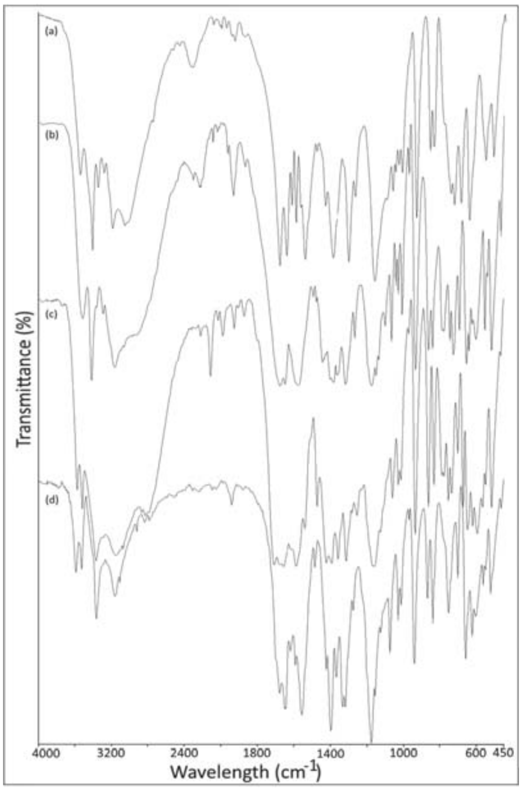
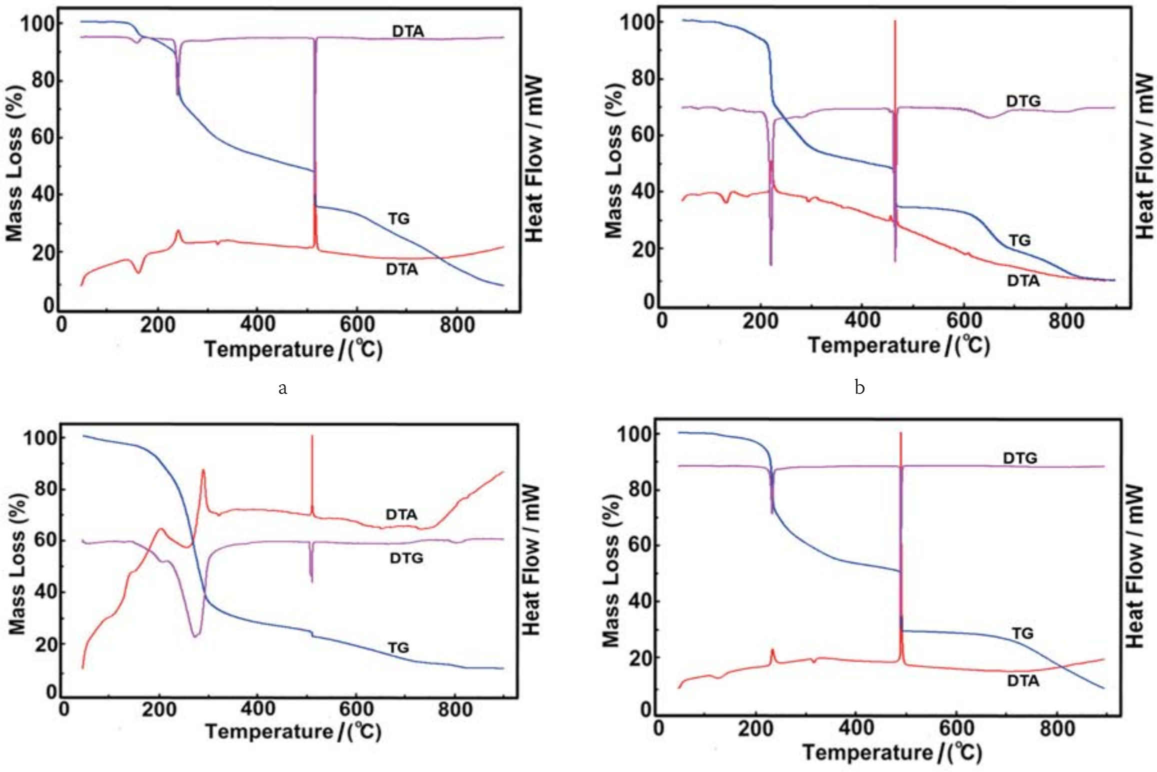


Figure 2. FT-IR spectra for a) $[Mg(H_2O)_4(na)_2](acs)_2$; b) $[Ca(H_2O)_6(na)_2](acs)_2$; c) $[Sr(H_2O)_7(na)_2](acs)_2$; d) $[Ba(H_2O)_7(na)_2](acs)_2$ complexes.



a

b

c

d

Figure 3. TG/DTG and DTA curves for a) $[Mg(H_2O)_4(na)_2](acs)_2$; b) $[Ca(H_2O)_6(na)_2](acs)_2$; c) $[Sr(H_2O)_7(na)_2](acs)_2$; d) $[Ba(H_2O)_7(na)_2](acs)_2$ complexes

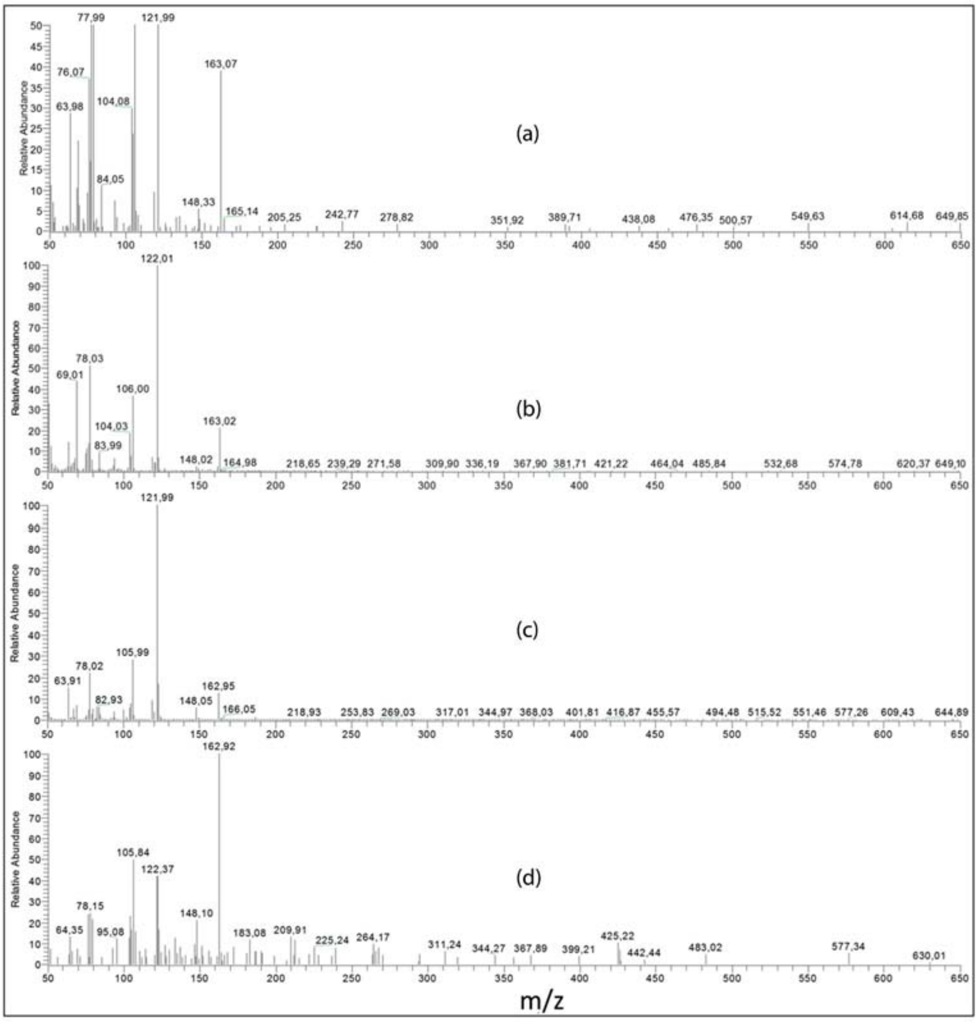


Figure 4. Mass spectra for a) $[Mg(H_2O)_4(na)_2](acs)_2$; b) $[Ca(H_2O)_6(na)_2](acs)_2$; c) $[Sr(H_2O)_7(na)_2](acs)_2$; d) $[Ba(H_2O)_7(na)_2](acs)_2$ complexes.

moles aqua ligand within its structure was subjected to two-step deaquation. 5.38% and 5.32% mass loss observed at the temperature range of 20-150°C and 150-214°C, respectively, are due to the leaving of two moles of aqua ligands (Theoretical: 5.4%). Next step is the leaving of nicotinamide ligands one by one. 18.43% and 18.34% mass losses observed at the temperature range of 214-234°C and 234-388°C, respectively, are due to the leaving of one mole of nicotinamide ligand (Theoretical: 18.37%). At this point, existence of $Mg(acs)_2$ was considered. The resulting compound was degraded at high temperature, and converted to MgO compound with leaving of organic part (acs) (Experimental: 5,97-Theoretical: 6.02%). Leaving of acesulfamate ions was corresponded to experimental mass of 45.6%. This value is theoretically 46.4%.

According to the thermal analysis curve belonging to $[Ca(H_2O)_6(na)_2]$ $(acs)_2$ complex given by Figure 3b, decomposition of structure was happened at two stages. The first stage is occurred at deaquation range corresponding to leaving of six mol aqua ligand (at 15-220°C range, Experimental: 14.7%, Theoretical: 14.2%), the second stage is the leaving of nicotinamide ligands (at 220-405°C range, Experimental: 33.97%, Theoretical: 34.05%). The final product corresponds to CaO compound (Experimental: 8.8%, Theoretical: 7.8%). From DTG curve, sharp peaks were observed where weight loss was happened. Therefore, it is evident for both the aqua and nicotinamide ligands are leaving from the complex structure very quickly.

Decomposition of $[Sr(H_2O)_7(na)_2](acs)_2$ structure takes place at two stages (Figure 3c). The first stage is deaquation. 7 moles of aqua ligand leave from the structure at the temperature range of 69-204°C (Experimental: 16.37% - Theoretical: 16.13%). The second stage is the leaving of nicotinamide which is the other neutral ligand. Two moles of nicotinamide are leaving from the structure at the temperature range of 204-255°C (Experimental: 31.26% - Theoretical: 31.23%). It is estimated that the final product is SrO compound. Broaden DTG curve shows that the leaving ligands are moving away from the structure slowly.

Thermal analysis curve for $[Ba(H_2O)_7(na)_2](acs)_2$ can be seen at Figure 3d. Complex decomposes at three steps. First stage of the decomposition is deaquation. Seven moles of aqua ligand are leaving at the temperature range of 25-223°C (Experimental: 15.05-Theoretical: 15.15%). The next stage of the decomposition is the leaving of 2 moles nicotinamide ligands at one step at the temperature range of 223-387°C (Experimental: 29.17% - Theoretical: 29.36%). At this stage, $Ba(acs)_2$ salt is formed. This salt was began to decompose at around 650°C. BaO compound is thought to be the final product (Experimental: 13.40% - Theoretical: 18.40%). From the DTG curve, there are sharp peaks where the weight loss was observed. This means that the leaving groups were moved away from the structure very quickly.

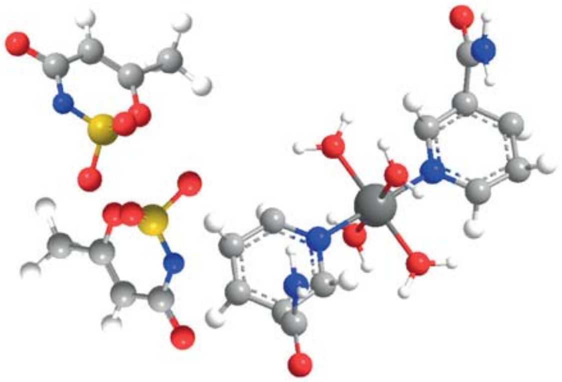


Figure 5. Proposed structure of $[Mg(H_2O)_4(na)_2](acs)_2$ complexes.

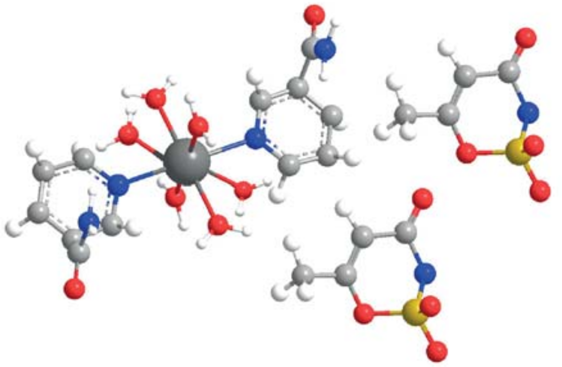


Figure 6. Proposed structure of $[Ca(H_2O)_6(na)_2](acs)_2$ complexes.

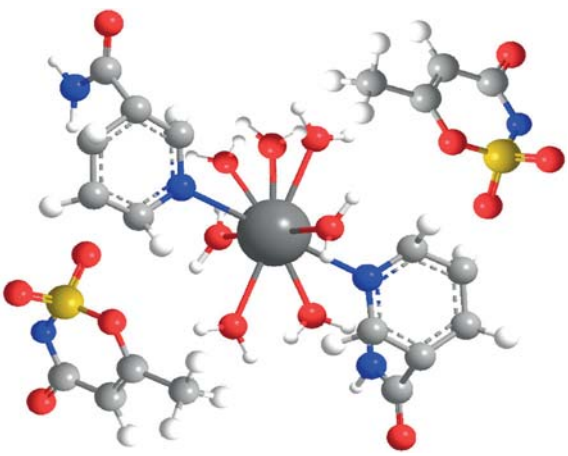


Figure 7. Proposed structure of $[Sr(H_2O)_7(na)_2](acs)_2$ and $[Ba(H_2O)_7(na)_2](acs)_2$ complexes.

Mass Spectra

Mass spectra for $[Mg(H_2O)_4(na)_2](acs)_2$, $[Ca(H_2O)_6(na)_2](acs)_2$, $[S(H_2O)_7(na)_2](acs)_2$ and $[Ba(H_2O)_7(na)_2](acs)_2$ complexes are given at Figure 4a, 4b, 4c and 4d, respectively. Moderate peaks with m/z ratio of 63.98; 64.00; 63.91 and 64.35 may be attributed to the leaving of SO_2 group. Peaks reason of which thought to be leaving of nicotinamide from metal-nicotinamide-acesulfame complexes are observed at 121.99, 122.01, 121.99 and 122.37 cm^{-1}, respectively. These peaks observed at mass spectra offer strong evidence for incorporation of ligands into coordination compounds.

CONCLUSIONS

Within the structure of complex, estimated 3D structure of which was given at Figure 5, 2 nicotinamide ligands were coordinated to Mg^{II} ions at trans position. For complex with octahedral geometry, while the other four coordinate was provided with aqua ligands, acesulfamato ions acted as counter-ions. From thermal analysis of the complex, it can be concluded that the decomposition was taken place through in order of leaving of two moles aqua, two moles aqua, a mole nicotinamide and a mole nicotinamide.

While Ca^{II} metal cation, coordination of which was estimated as 8, completes coordination through 2 moles of nicotinamide ligand and 6 moles of aqua, +2 charged cation was balanced with 2 moles acesulfamate anions acting as counter ion (Figure 6).

Coordinations of complexes formed by isostructural Sr^{II} and Ba^{II} metal cations was completed to 9 through seven moles of aqua and 2 moles of nicotinamide ligands (Figure 7). The charge balance of metals was ensured through mono-anionic acesulfamate anions located outside of coordination sphere as done in other complex structures. Conductivity tests were performed to determine whether acesulfamate anions act as counter-ion for all complexes, and structures are salt-type complex structures.

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