

Crystal Structure, Thermal Analysis, Spectroscopic Studies and DFT Calculations on Hexaaquamagnesium(II) Acesulfamate

Hekzaaquamagnezyum(II) Asesulfamat Molekülünün Kristal Yapısı, Termal Analizi, Spektroskopik Çalışmaları ve DFT

Research Article

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ABSTRACT

The crystal structure of the complex, $[Mg(H_2O)_6](C_4H_4NO_4S)_2$, was determined at 296 K. The unit cell parameters of the crystal structure are $a=6.9404 \text{ \AA}$, $b=8.5775 \text{ \AA}$, $c=8.7200 \text{ \AA}$, $\alpha=68.564^\circ$, $\beta=78.640^\circ$, $\gamma=81.260^\circ$ and $Z=1$. The complex crystallizes in the centrosymmetric triclinic space group P-1. The Mg(II) ion is coordinated by six O atoms from six aqua ligands and in the crystal structure, the anions and cations are linked with three dimensions via O-H...O and O-H...N interactions. In addition to the structure which was obtained by X-ray diffraction technique, the theoretical structure was calculated by using density functional theory (B3LYP) with the 6-31G basis sets. The molecular electrostatic potential, frontier molecular orbitals and theoretical IR studies were calculated by using DFT method. Besides, the experimental IR spectrum and thermal analysis were investigated for the complex.

Key Words

Magnesium; DFT Calculations; Coordination Chemistry; Crystal Structure, Thermal Characterization.

ÖZET

Kompleksin kristal yapısı $[Mg(H_2O)_6](C_4H_4NO_4S)_2$, 296 K'de tayin edildi. Moleküler Kristal yapının birim hücre parametreleri $a=6.9404 \text{ \AA}$, $b=8.5775 \text{ \AA}$, $c=8.7200 \text{ \AA}$, $\alpha=68.564^\circ$, $\beta=78.640^\circ$, $\gamma=81.260^\circ$ ve $Z=1$ olarak saptanmıştır. Kompleks merkezi simetrik triklinik yapıda kristallenmiş olup uzay grubu P-1'dir. Her bir Mg(II) iyonu altı mol su ligandının O atomları tarafından koordine edilmiştir. Kristal yapıda anyonlar ve katyonlar O-H...O ve O-H...N etkileşimleriyle üç boyutlu yapıyı oluştururlar. İlave olarak yoğunluk fonksiyonel teori (DFT) (B3LYP) yönteminin 6-31G temel setleri kullanılarak elde edilen hesaplanmış sonuçlarla deneysel X-ışınları kırınım sonuçları kıyaslanarak moleküler yapı oluşturulmuştur. Moleküler elektrostatik potansiyel, frontier moleküler orbitaller ve IR spektrumu DFT yöntemi kullanılarak hesaplanmıştır. Ayrıca, deneysel IR spektroskopisi ve termal analiz yöntemleri ile yapı incelenmiştir.

Anahtar Kelimeler

Magnezyum; DFT Hesaplamaları; Koordinasyon Kimyası; Kristal Yapı; Termal Karakterizasyon.

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INTRODUCTION

Acesulfame (acs) is without calorie and has been used as artificial sweetener since 1988. Acesulfame is not digested, accumulated and changed in the human metabolism and it is rapidly excreted from the body [1]. While acesulfame with some ammonium compounds exhibits acute oral toxicities, deterrent activity and causes skin irritation, choline acesulfamate has low toxic character [2,3]. In addition biological importance of acesulfame, its coordination characteristics are also important, since acesulfame has donor atoms which can form coordination bonds with metal ions [4]. Studies belong to the different crystalline forms of acesulfame, which may have different physical, chemical and mechanical properties, have been reported in the literature [5].

The coordination compounds of s-block elements are preferred to transition or lanthanide metal ions, because alkali and alkali earth metals are cheap and soluble in aqueous media and have non-toxic properties [6]. Magnesium, which is very important biologically in alkali earth metals, has been reported in three different states in most biological system. These are bounded to protein, complexed to anion and free [7]. It is fundamental for the regulation of various biological processes. The magnesium deficiency especially may play a crucial role in pathogenesis of ischemic heart disease, cardiomyopathy, and certain arrhythmias [7-11]. In this study, the crystallographic, spectroscopic and theoretical studies of hexaaquamagnesium(II) acesulfamate complex was handled.

Experimental

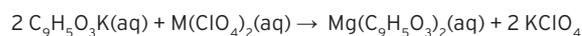
Material Methods

All chemicals were obtained from Sigma-Aldrich and used without purification. Elemental analysis (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). IR spectra were recorded in the 4000-400 cm^{-1} region with a Perkin Elmer Spectrum One FTIR spectrophotometer using KBr pellets. Thermal analyses (TGA, DTA) were performed by the

Shimadzu DTG-60H system, in dynamic nitrogen atmosphere (100 mL/min) at a heating rate of 10°C/min, in platinum crucibles as sample vessel, using $\alpha\text{-Al}_2\text{O}_3$ as reference. Mass spectra was recorded Thermo Scientific DSQ II Single Quadrupole GC/MS in the electron impact (EI) ionisation mode (70 eV) and HP-5MS (bonded and cross-linked 5% phenyl-methylpolysiloxane, 30 mm x 0.25 mm, coating thickness 0.25 μm) capillary column (Restek, Bellefonte, PA). The single XRD data was collected by a STOE IPDS II diffractometer equipped with a graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K.

Synthesis of Metal-Acesulfame (ace) Complexes

A hot solution (60°C) of acesulfame potassium salt (8 mmol, 1.610 g) in distilled water (50 mL) was gradually added to a hot stirring solution of magnesium perchlorate dihydrate ($\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$) (4 mmol, 1.037 g) in distilled water (50 mL). The obtained mixture was stirred on a hot plate with slow evaporation to dryness at 70°C. The complex was extracted with absolute ethanol from the resulting precipitate consisting of both itself and KClO_4 salt according to the below reaction scheme.



The final ethanolic solution was left for crystallization and in a few days, the crystals of X-ray quality were obtained by slow evaporation from the solution at room temperature.

Theoretical Study

The geometrical parameters were calculated using the Gaussian 03 program package and B3LYP approach in conjunction with the 6-31G (d,p) basis set [12]. For modeling, the X-ray coordinates were used as the initial values.

For the harmonic vibrational frequencies, the same level of theory had been used for finding the optimized structure and the obtained frequencies were scaled by 0.9627 [13]. The vibrational bands assignments were made by using Gauss-View molecular visualization program [14].

Table 1. Analytical data of MgII and CaII complexes.

Compound	MA (g/mol)	m.p.* (°C)	C (%)		H (%)		N (%)		S (%)	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$C_8H_{20}MgN_2O_{14}S_2$	456.69	95	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
			21.93	21.04	5.26	4.40	6.07	6.14	14.04	13.72

RESULT and DISCUSSION

The analytical data of complexes were given in Table 1. The yield of compounds are about 82% for MgII complex and 87% for CaII complex.

X-Ray Crystal Structure Determination

Single-crystal X-ray data were collected on a Stoe IPDS II single crystal diffractometer using monochromated MoK α radiation at 296 K. X-AREA and X-RED programs were used to cell refinement and data reduction, respectively [15]. SHELXS-97 and SHELXL-97 programs were used to solve and refine the structure, respectively [16]. ORTEP-3 for Windows was used to preparation the figures [17]. WinGX and PLATON software were used to prepare material for publication [18,19]. The same molecular structure $C_8H_{20}MgN_2O_{14}S_2$, explained by Piro and co-authors [20], the single crystal structure of $C_8H_{20}MgN_2O_{14}S_2$ was studied again for compare with theoretical results.

All of the hydrogen atoms were positioned freely. The C–H bond distances are 0.95 (2) Å, 0.95 (3) Å and 0.91 (3) Å for methyl group and 0.93 (2) Å for aromatic C–H. The O–H bond distances range from 0.79 (3) Å to 0.87 (3) Å for aqua ligands. The refinement parameters of the crystal structure are given in Table 2.

The hexaaquamagnesium(II) acesulfamate molecule crystallizes in the centrosymmetric triclinic space group P-1. The unit cell of the complex contains one $[Mg(H_2O)_6]^{2+}$ dication and two $(acs)^-$ anions. As can be seen in Figure 1, the Mg^{2+} ion has six-coordination by six O atoms from six aqua ligands and the environment of Mg^{2+} has distorted octahedron geometry. The Mg–O bond distances range from 2.0445 (11) Å to 2.0817 (12) Å. These values are consistent

with the literature [21-23]. The C1–N1 and C1–O4 bond distances and C1–N1–S1 bond angle are 1.3448 (19) Å, 1.2472 (18) Å and 119.71 (10)°, respectively. The bond distances and bond angles of some acs complexes have been reported for $[Ni(acs)_2(H_2O)_4]$ [4] (i.e., the C1–N1, C1–O1 and C1–N1–S1 are 1.338 (2) Å, 1.258 (2) Å and 118.66 (10)°), for $[Cu(C_4H_4NO_4S)_2(C_4H_5N_3)_2]$ [24] (i.e., the C1–N1 and C1–O1 are 1.333 (3) Å and 1.274 (2) Å), for $[Co(C_4H_4NO_4S)_2(H_2O)_4]$ [25] (i.e., the C1–N1, C1–O1 and C1–N1–S1 are 1.361 (3) Å, 1.251 (3) Å and 117.65 (16)°), for $[Cd_2(C_4H_4NO_4S)_2(C_6H_7N)_2]$ [26] (i.e., the C17–O5 and C13–O4 are 1.254 (3) Å and 1.244 (4) Å), for $[Cu(dmen)_2(H_2O)_2](acs)_2$ [27] (i.e., the C5–N3–S is 123.0 (2)°), $[Ca_2(acs)_2(H_2O)_2(acs)_2]_n$ [28] (i.e., the C4 N1, C5 N2, C4 N1 S1, C5 N2 S2 are 1.334 (2) Å, 1.337 (2) Å, 119.18 (11)° and 119.09 (11)°, respectively). The O–Mg–O bite angles of the complex range from 88.59 (5)° to 180.00 (7)°.

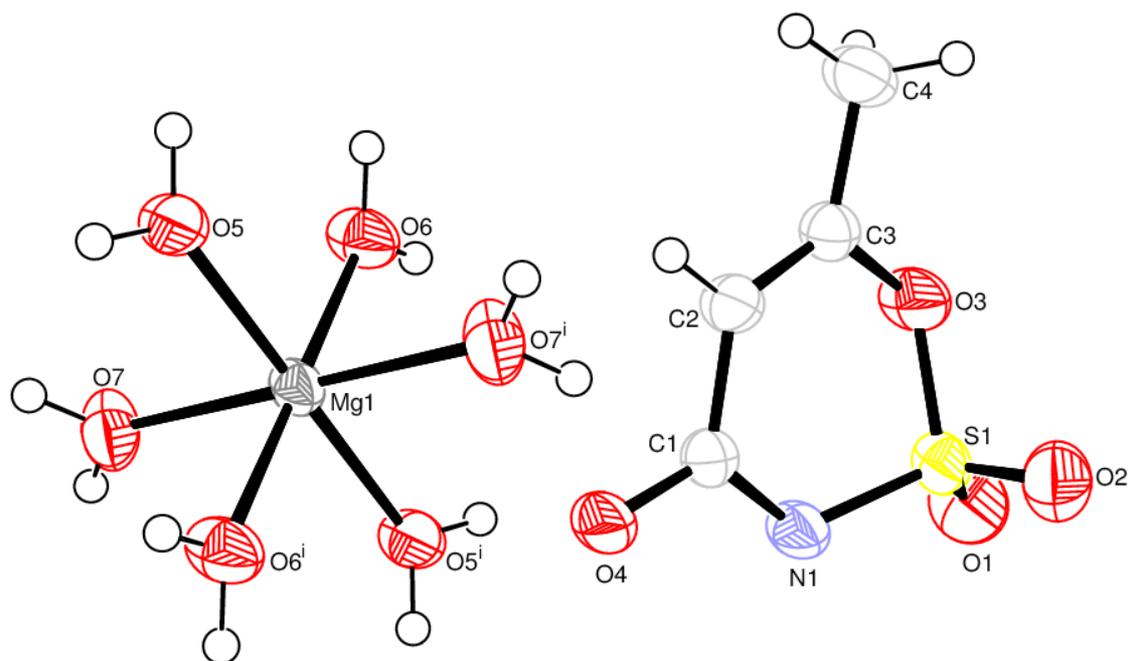
In the crystal structure, $(acs)^-$ anions and water molecules are linked through O–H \cdots O and O–H \cdots N hydrogen bonds into three dimensions framework. The geometric parameters of some hydrogen bonds are 0.84 (3) Å, 1.85 (3) Å, 2.6909 (18) Å and 177 (3)° for O5–H5A \cdots O4; 0.84 (3) Å, 1.86 (3) Å, 2.6960 (19) Å and 173 (2)° for O7–H7B \cdots O4, respectively. The detailed geometric parameters of hydrogen bonds are given in Table 3.

As can be seen in Figure 2, the $[Mg(H_2O)_6]^{2+}$ dications settle to the corner of unit cell, while the $(acs)^-$ anions are settling to the center of unit cell. These anions and cations are linked through hydrogen bonds in the crystal structure.

In complex cation, the Mg1–O5, Mg1–O6 and Mg1–O7 bond distances are 2.0445 (11) Å, 2.0644 (12) Å and 2.0817 (12) Å, respectively. Because

Table 2. Crystal data and structure refinements of the complex.

Formula	$C_8H_{12}OMgN_2O_{14}S_2$
Formula weight	456.69
Crystal system	Triclinic
Space group	P-1
Unit cell Dimensions (\AA , $^\circ$)	
a,b,c	6.9404 (8), 8.5775 (11), 8.7200 (12)
α , β , γ	68.564(10), 78.64(1), 81.26(1)
Volume (\AA^3), Z	471.92 (10), 1
F(000)	238
Range for collection data ($^\circ$)	2.54-27.41
Limiting indicatcs	$-8 \leq h \leq 8$; $-10 \leq k \leq 10$; $-10 \leq l \leq 10$
Collected Reflections	8556
Independent reflections	[R(int)=0.0431] 1858
Completeness (%)	100
Goodness-of-fit on F^2	1.0880
Final R indices [$I > 2\sigma(I)$]	$R_1=0.027$; $wR_2=0.076$
R indices (all data)	$R_1=0.031$; $wR_2=0.078$

**Figure 1.** ORTEP diagram of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. $i = -x, -y, -z$.

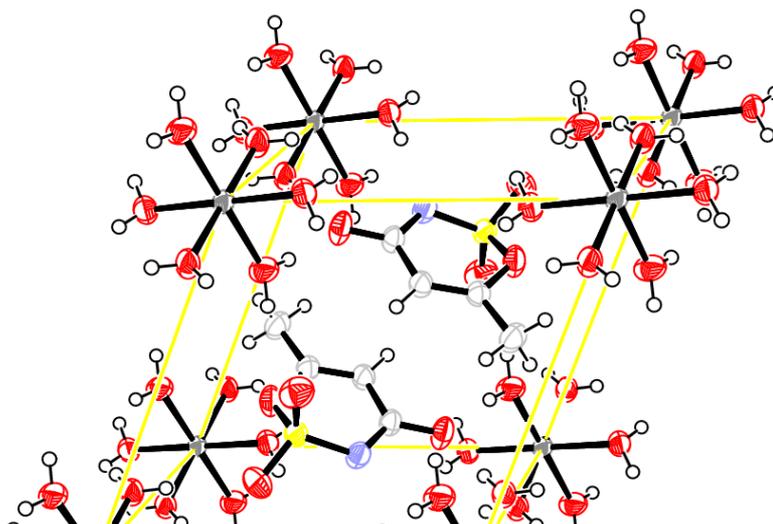


Figure 2. The crystal packing of the title compound in the unit cell.

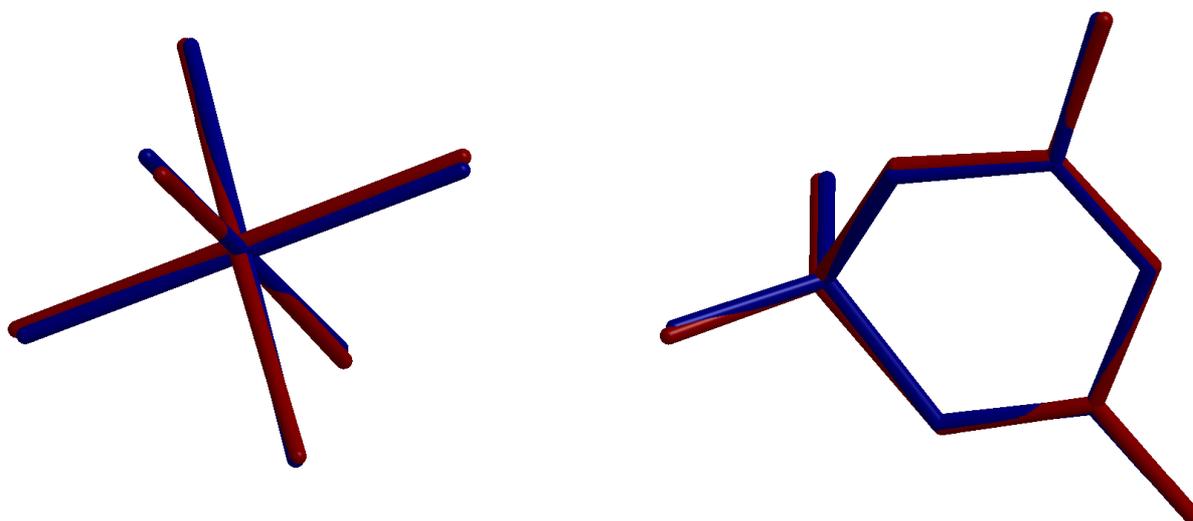


Figure 3. Atom-by-atom superimposition of the structures calculated (red) (DFT B3LYP/6-31G(d,p)) on the x-ray structure (blue) of the title compound (r.m.s.=1.569). Hydrogen atoms have been omitted for clarity.

of these bond distances are almost equal, the environment of Mg^{2+} ion deviates very little from octahedron geometry.

Theoretical Results

While the least difference between experimental and theoretical bond distances is between C1 and N1 atoms with 0.0001 Å, the biggest difference between experimental and theoretical bond distances is between O3 and S1 atoms with 0.1261 Å. The experimental (blue) and theoretical (red) structures of the complex are given in Figure

3. The theoretical and experimental molecular geometries are approximately superposed.

In the crystal structure, the experimental and theoretical Mg–O bond distances are found 2.0445 (11) Å and 2.1456 Å for Mg1–O5i; 2.0445 (11) Å and 2.1055 Å for Mg1–O5; 2.0644 (12) Å and 2.1006 Å for Mg1–O6i; 2.0644 (12) Å and 2.119 Å for Mg1–O6; 2.0817 (12) Å and 2.117 Å for Mg1–O7i; 2.0817 (12) Å and 2.099 Å for Mg1–O7, respectively. Although the Mg–O bond distances defined by X-ray diffraction technique equal

to each other symmetrically, the Mg–O bond distances calculated by DFT method are different from each other symmetrically, due to only one molecule was calculated by DFT. If bond angles are considered, the biggest difference between experimental and theoretical bond angles are found for O5–Mg1–O6i with 13.4619°. The least difference between experimental and theoretical bond angles are found for O1–S1–O3 with 0.0112°. The experimental and theoretical bond distances, bond angles, torsion angles and the error quantities between experimental and theoretical values are given in Table 4.

While the biggest difference between experimental and theoretical torsion angles is found for C3–O3–S1–O1 with 6.0164°, the least difference between experimental and theoretical torsion angles is found of C1–N1–S1–O2 with 0.9412°.

In this study, we looked accordance between theoretical and experimental values and couldn't find large difference between the theoretical and experimental values.

Frontier Molecular Orbitals

The LUMO+1, LUMO, HOMO, HOMO-1 orbitals were calculated for the complex and the energy levels with distributions of these molecular orbitals were given in Figure 4. While HOMO and LUMO+1 are not localized on acs ligand, HOMO-1 is only localized on acs ligand. Electrons are delocalized on the water molecules that surrounded Mg²⁺ ion at HOMO and LUMO+1 orbitals. The energy gap between HOMO and LUMO is 1.3984 eV.

Molecular Electrostatic Map

The molecular electrostatic potential map (MEP) was calculated for the structure which is optimized with B3LYP/6-31G(d,p). The values of MEP which correspond to the surface determined from points with electronic density (ρ) 0.0004 a.u. were used. The negative regions of the MEP are related to electrophilic reactivity and positive regions are related to nucleophilic reactivity.

Molecular electrostatic potential (MEP) indicates electrophilic and nucleophilic attack centers as well as intermolecular interactions

such as hydrogen bonding interactions [29,30] As shown in Figure 5, the molecule has a few nucleophilic attack centers. The maximum nucleophilic regions are at the environment of H5A and H7A atoms with approximately 0.0605 a.u. and 0.0531 a.u., respectively. The electrophilic regions for the molecule are at the environment of O1 and O2 atoms with approximately -0.0591 a.u. and -0.0605 a.u., respectively. The crystal structure has six hydrogen bonds, all of these hydrogen bonds which are between [Mg(H₂O)₆]²⁺ dications and (acs)⁻ anions are concentrated at vicinity of nucleophilic attack center and electrophilic attack center. Additionally, the dipole moment and total energy of the title compound were found as 7.0927 D and -1567.4032 a.u.

Vibrational Spectrum

The theoretical and experimental vibrational frequencies of the hexaaquamagnesium(II) acesulfamate between 550 cm⁻¹ and 4000 cm⁻¹ are seen in Figure 6.

Theoretical stretching frequencies for H₂O molecules range also from 3014.98 cm⁻¹ to 3689.18 cm⁻¹. These stretching vibrational frequencies are observed as broaden curve at around 3570 cm⁻¹ and 3546 cm⁻¹ experimentally. Theoretical scissoring frequencies for H₂O molecules range from 1467.27 cm⁻¹ to 1658.57 cm⁻¹. Hydrogen bonds are a very important effect in infrared spectroscopy [31] and the aqua ligands surrounded Mg²⁺ ion make many hydrogen bonds with other molecules, therefore the spectrum is broaden. Theoretical stretching vibrational frequencies belong to C=O and C=C were found at 1468.62 cm⁻¹ and 1614.33 cm⁻¹, respectively. The experimental spectrum for C=O and C=C may be at about 1655 cm⁻¹ and 1554 cm⁻¹. The carbonyl stretching band of K(acs), [Co(acs)₂(H₂O)₄] and [Ni(acs)₂(H₂O)₄] had been found at 1661 cm⁻¹, 1656 cm⁻¹ and 1653 cm⁻¹, respectively [4]. While theoretical symmetric SO₂ stretching frequencies are calculated at 1126.65 cm⁻¹, experimental SO₂ stretching vibrations are seen at 1161.63 cm⁻¹ and 1169.24 cm⁻¹. Theoretical asymmetric SO₂ stretching frequencies were calculated at 1312.07 cm⁻¹. The experimental asymmetric SO₂ stretching vibrations were detected at 1307.86 cm⁻¹ and 1278.92 cm⁻¹. These values had been

Table 4. Experimental and theoretical bond distances, bond angles and torsion angles (Å,°).

Atoms	X-Ray	Theoretical	Error
C1-O4	1.2472 (18)	1.2858	-0.0386
C1-N1	1.3448 (19)	1.3449	-0.0001
C1-C2	1.455 (2)	1.4516	0.0034
C2-C3	1.326 (2)	1.3543	-0.0283
C3-O3	1.3862 (18)	1.3548	0.0314
C3-C4	1.477 (2)	1.4948	-0.0178
Mg1-O5i	2.0445 (11)	2.1456	-0.1011
Mg1-O5	2.0445 (11)	2.1055	-0.0610
Mg1-O6i	2.0644 (12)	2.1006	-0.0362
Mg1-O6	2.0644 (12)	2.119	-0.0546
Mg1-O7i	2.0817 (12)	2.117	-0.0353
Mg1-O7	2.0817 (12)	2.099	-0.0173
N1-S1	1.5648 (13)	1.6228	-0.0580
O1-S1	1.4224 (13)	1.4516	-0.0292
O2-S1	1.4224 (14)	1.4578	-0.0354
O3-S1	1.6064 (12)	1.7325	-0.1261
O4-C1-N1	119.52 (13)	117.4629	2.0571
O4-C1-N1	119.52 (13)	117.4629	2.0571
N1-C1-C2	119.92 (13)	122.9148	-2.9948
C3-C2-C1	123.00 (14)	122.0115	0.9885
C2-C3-O3	121.01 (13)	123.0256	-2.0156
C2-C3-C4	127.88 (15)	125.2354	2.6446
O3-C3-C4	111.11 (13)	111.7168	-0.6068
O5i-Mg1-O5	180.00 (7)	174.654	5.3460
O5i-Mg1-O6i	90.78 (5)	82.6229	8.1571
O5-Mg1-O6i	89.22 (5)	102.6819	-13.4619
O5i-Mg1-O6	89.22 (5)	82.9244	6.2956
O5-Mg1-O6	90.78 (5)	91.7345	-0.9545
O6i-Mg1-O6	180.00 (11)	164.858	15.142
O5i-Mg1-O7i	88.59 (5)	87.9714	0.6186
O5-Mg1-O7i	91.41 (5)	91.5257	-0.1157
O6i-Mg1-O7i	90.80 (5)	87.9752	2.8248
O6-Mg1-O7i	89.20 (5)	87.0229	2.1771
O5i-Mg1-O7	91.41 (5)	94.7096	-3.2996

Table 4. Experimental and theoretical bond distances, bond angles and torsion angles (Å,°) (Continue).

O5-Mg1-O7	88.59 (5)	85.3799	3.2101
O6i-Mg1-O7	89.20 (5)	96.8848	-7.6848
O6-Mg1-O7	90.80 (5)	88.7785	2.0215
O7i-Mg1-O7	180.00 (9)	174.708	5.2920
C1-N1-S1	119.71 (10)	120.0601	-0.3501
C3-O3-S1	117.39 (9)	118.0919	-0.7019
O1-S1-O2	116.30 (9)	120.0263	-3.7263
O1-S1-N1	110.26 (8)	110.5333	-0.2733
O2-S1-N1	112.79 (8)	112.1907	0.5993
O1-S1-O3	103.55 (8)	103.5388	0.0112
O2-S1-O3	106.37 (8)	104.4441	1.9259
N1-S1-O3	106.61 (7)	104.2713	2.3387
O4-C1-C2-C3	-172.61 (16)	-168.5696	-4.0404
N1-C1-C2-C3	5.9 (2)	8.1742	-2.2742
C1-C2-C3-O3	-1.1 (2)	-3.9296	2.8296
C1-C2-C3-C4	178.22 (16)	174.2134	4.0066
O4-C1-N1-S1	-166.15 (12)	-170.2983	4.1483
C2-C1-N1-S1	15.4 (2)	12.8941	2.5059
C2-C3-O3-S1	-23.3 (2)	-18.9379	-4.3621
C4-C3-O3-S1	157.26 (12)	162.6946	-5.4346
C1-N1-S1-O1	-146.67 (14)	-140.7135	-5.9565
C1-N1-S1-O2	81.47 (15)	82.4112	-0.9412
C1-N1-S1-O3	-34.91 (15)	-30.0292	-4.8808
C3-O3-S1-O1	155.09 (12)	149.0736	6.0164
C3-O3-S1-O2	-81.83 (13)	-84.5189	2.6889
C3-O3-S1-N1	38.76 (13)	33.3828	5.3772

reported at 1195 cm⁻¹ for [Co(acs)₂(H₂O)₄] and 1194 cm⁻¹ for [Ni(acs)₂(H₂O)₄] [4]. The theoretical C-O and S-O stretching frequencies were calculated at 940.76 cm⁻¹ and 653.58 cm⁻¹, respectively. The experimental spectrums belong to these stretching vibrations were found at 1073.27 cm⁻¹ and 841.73 cm⁻¹, respectively.

Thermal Analysis

TG, DTG and DTA plots and significant degradation steps for [Mg(H₂O)₆](acs)₂ complex are given by Figure 7. The first step of the thermal analysis plot of [Mg(H₂O)₆](acs)₂ complex is the removal of

hydrated water (as moisture).

At first step corresponding to the temperature range of 0-95.42°C, approximately 1 mole of water is removed (Experimental: 3.29%, Theoretical: 3.94%). Subsequent 3 steps are deaquation. The first step of deaquation is observed at the temperature range of 95-164°C by the weight loss of 8.22%. This loss is due to the removal of 2 moles of aqua ligands (Theoretical: 7.88%).

8.18% weight loss observed at the temperature range of 164-213°C is the second

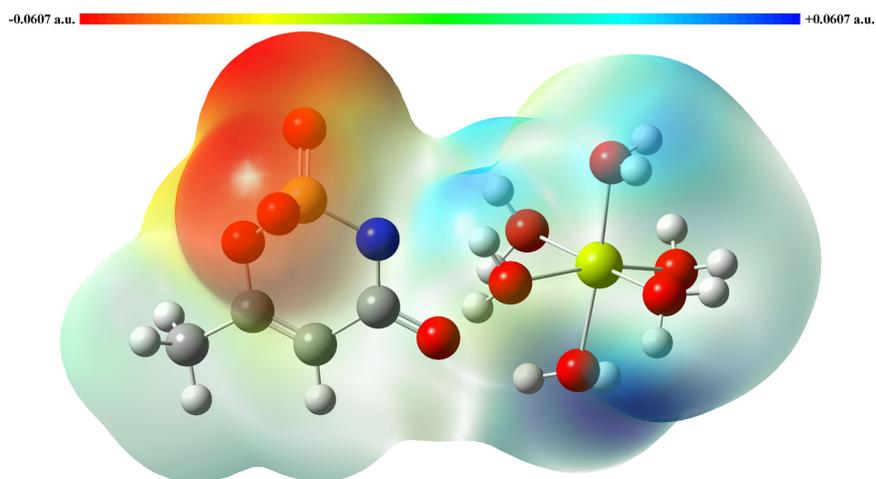


Figure 5. Molecular electrostatic potential map at the B3LYP/6-31G(d,p) level.

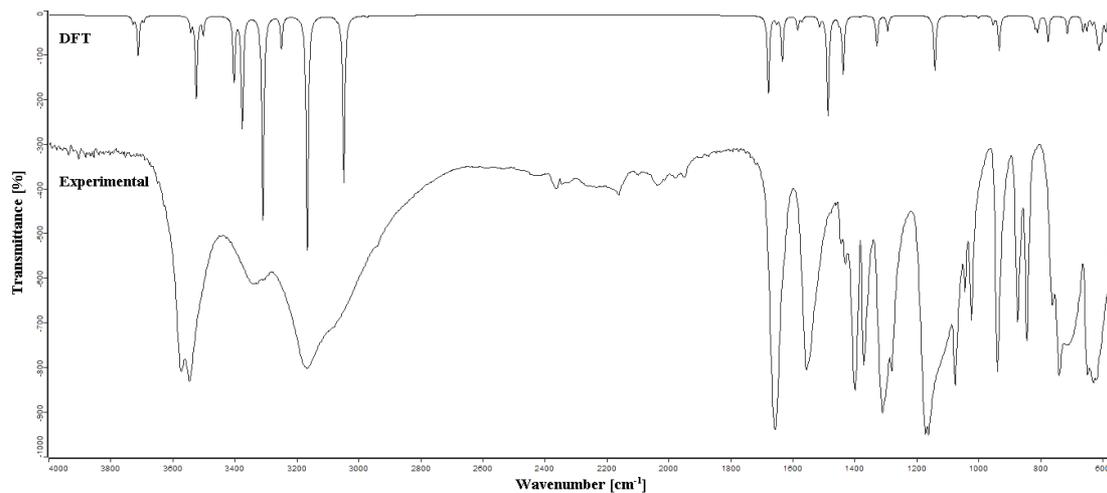


Figure 6. The theoretical and experimental spectrum of the title compound.

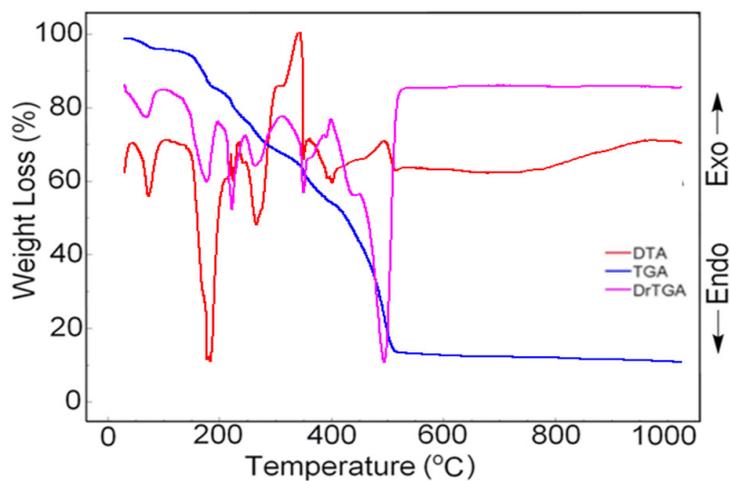


Figure 7. The TG, DTG and DTA curves of the $[\text{Mg}(\text{H}_2\text{O})_6](\text{acs})_2$ complex.

Table 5. Thermoanalytical results (TG-DTG/DTA) for the metal complexes.

Complex	Temp. Range/C	DTA _{max} / °C	Removed Group	Weight Change/%		Total Loss/%		Decom. Prod.	Colour
				Found	Calc.	Found	Clac.		
C ₈ H ₂₀ MgN ₂ O ₁₄ S ₂				Found	Calc.	Found	Clac.		White
	1	45-65	55	2/3 H ₂ O*	2.46	2.63			
	2	97-174	166	2 H ₂ O	7.57	7.01			
	3	176-220	211	2 H ₂ O	7.12	7.01			
	4	232-282	251	2 H ₂ O	6.74	7.01			
	5	290-352	-315.335	SO ₂	14.43	14.02			
	6	354-429	385	SO ₂	13.65	14.02			
7	430-523	448.498	C ₄ H ₄ NO ₂ ,C ₄ H ₄ N	38.77	39.41	9.26	8.89	MgO	Gray

step of deauration. Also at this stage, 2 mol of aqua ligand are removed (Theoretical 7.88%).

The final step of deauration is occurred at the temperature range of 213-256°C. Weight loss of 8.04% corresponds to removal of 2 moles of aqua ligand. After this step, it is considered that Mg(acs)₂ is formed.

An exothermic weight loss of 14.13% is observed at the temperature range of 290-352°C. This loss corresponds to removal of SO₂ due to the decomposition of one of acs ligands (Theoretical: 14.01%). At 354-429°C, there is also an exothermic mass loss of 13.934% observed. This is the decomposition of the other acs ligands and SO₂ removal. It is thought that endothermic mass loss of 38.77% occurred at the temperature range of 430-523°C is because of the removal of organic residue formed as a result of the decomposition of organic ligands. Remaining MgO as a decomposition product is determined by infrared spectroscopy. Our idea is supported by that experimental residue amounts investigated are in accordance with the theoretical values (exp.: 9.26% - calc.: 8.89%). DTG plot shows that aqua ligands are removed step by step as stated above. The color of last decomposition product is grayish because of not fully completed combustion depending on analysis to be carried out in an inert nitrogen atmosphere and remaining carbonized carbon on the surface of residue product.

The thermal decomposition steps, removed products and decomposition temperature range of both of are summarized at Table 5.

The crystal structure data show that the [Mg(H₂O)₆](acs)₂ complex has three different aqua ligands having different bond lengths [Mg-O(H₂O): 2.0445 (11) Å, 2.0644 (12) Å, 2.0817 (12) Å]. The deauration process of the [Mg(H₂O)₆](acs)₂ complex occurs at three steps that agree with the crystal data.

Mass Analysis

The thermal decomposition pathway of the [Mg(H₂O)₆](C₄H₄NO₄S)₂ complex was recorded using direct insertion probe pyrolysis mass spectrometry method (Figure 8). The thermal decomposition pathway of the [Mg(H₂O)₆](C₄H₄NO₄S)₂ complex was recorded using direct insertion probe pyrolysis mass spectrometry method (Figure 8). The mass spectra show the fragmentation pattern and the most fragile points of the molecule. The molecular ion peaks in the mass spectra recorded were detected at the 455.55. Beside the most abundant peaks, much fewer abundant peaks observed on the spectra depend probably on the nature of ligands.

Conclusion

The hexaaquamagnesium(II) acesulfamate complex consists of [Mg(H₂O)₆]²⁺ dication and (acs)⁻ anion. In the crystal structure, [Mg(H₂O)₆]²⁺ dications and (acs)⁻ anions have been linked

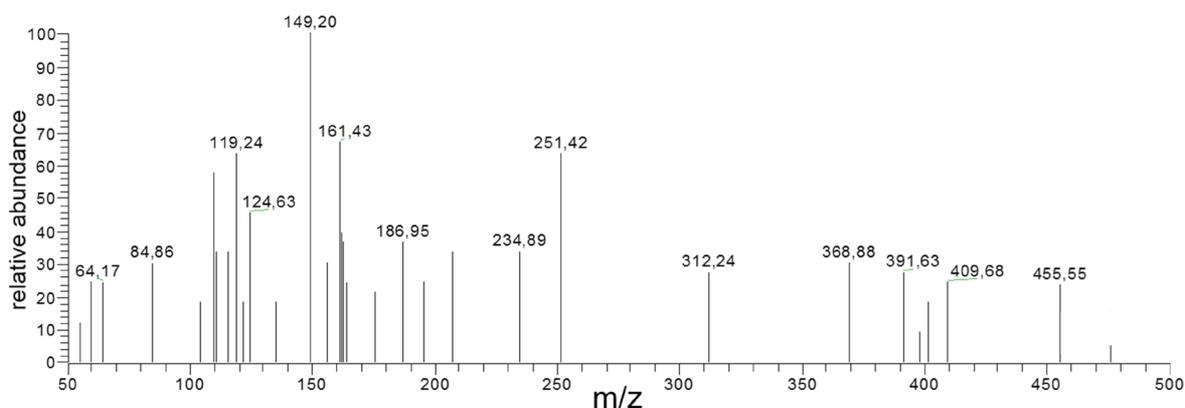


Figure 8. Solid Probe GC-Mass Spectroscopy pattern of $\text{Mg}(\text{H}_2\text{O})_6[(\text{C}_4\text{H}_4\text{NO}_4\text{S})_2]$ complex.

through O–H...O hydrogen bonds. The geometric parameters obtained by x-ray diffraction are very close to the theoretical geometric parameters for magnesium complex.

The environment of Mg^{2+} ion with coordinated six aqua ligands has distorted octahedron geometry. The energy gap between HOMO and LUMO has found 1.3984 eV for magnesium complex with B3LYP/6-31G(d,p).

As shown at MEP, while the electrophilic attack centers of this complex are at the environment of sulfonyl oxygen, the nucleophilic attack centers are at the environment of hydrogen atoms belong to aqua ligands. The intermolecular hydrogen bonds are shown at these regions from information obtained by x-ray diffraction.

The vibrational frequencies belong to magnesium complex show some deviation from other reported crystal structures [4], because of different molecular geometry. The reason of difference between theoretical and experimental values may be hydrogen bonds and different geometric parameters between experimental and theoretical structure.

Thermal analysis of the complex is compatible with the structure determined by X-ray technique. The six aqua ligands decompose with three stages from molecule. At the last, SO_2 group release from complex and final product, MgO , remains left over from behind [32-34].

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