EXPERIMENTAL AND THEORETICAL (DFT) STUDIES OF POLY[OCTA-μ_3-ACESULFAMATO-*O,O*:*N,O'*;*O'*,*N*:*O,O*-TETRAAQUATETRABARIUM(II)] AND POLY[OCTA-μ_3-ACESULFAMATO-*O,O*:*N,O'*;*O'*, *N*:*O,O*-TETRAAQUATETRASTRONTIUM(II)] COMPLEXES[†]

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Two new one-dimensional coordination polymers of barium(II) and strontium(II)-acesulfamato complexes such as [Ba(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]$_n$ (1) and [Sr(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]$_n$ (2) have been synthesized and their molecular structures were identified by X-ray diffraction technique. Both barium(II) and strontium(II) complexes crystallize in the centrosymmetric monoclinic space group P12$_1$/c1 and barium(II) and strontium(II) ions, which are surrounded by *O*- and *N*-atoms, have the coordination number of nine. Each complex forms a structure like a polymer extending parallel to the *a*-axis. The molecular structures of those complexes were stabilized by O—H···O and C—H···O hydrogen bonds.

Besides identifying their crystallographic structures, the geometric parameters were also calculated using density functional theory (B3LYP) with 6-31G base sets for the asymmetric units of the complexes. The calculated geometrical parameters were also compared to the geometric parameters of X-ray diffraction technique. Furthermore, molecular electrostatic potential maps were constructed and frontier molecular orbital calculations were done for the synthesized complexes. The results of the experimental and theoretical IR studies were also compared.

Keywords: acesulfamato ligand; barium(II) complex; strontium(II) complex; density functional theory

ЕКСПЕРИМЕНТАЛНИ И ТЕОРЕТСКИ (DFT) ИСТРАЖУВАЊА НА КОМПЛЕКСИ НА ПОЛИ[ОКТА-μ_3-АЦЕСУЛФАМАТО-*O,O*:*N,O'*;*O'*,*N*:*O,O*-ТЕТРААКВАТЕТРАБАРИУМ(II)] И ПОЛИ[ОКТА-μ_3-АЦЕСУЛФАМАТО-*O,O*:*N,O'*;*O'*,*N*:*O,O*-ТЕТРААКВАТЕТРАСТРОНЦИУМ(II)]

Со помош на рендгенска дифракција се синтетизирани и определени молекулските структури на два нови еднодимензионални координациони полимери на комплексите на бариум(II)- и стронциум(II)-ацесулфамати од типот [Ba(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]$_n$ (1) и [Sr(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]$_n$ (2). Комплексите на бариум(II) и стронциум(II) кристализираат во центросиметричната моноклинична просторна група P12$_1$/c1, и јоните на бариум(II) и стронциум(II) јоните, кои се опкружени со *O*- и *N*-атоми, имаат координатен број девет. Секој од комплексите формира полимерна структура која се простира надолж оската *a*. Молекулските структури на овие комплекси се стабилизирани со водородни врски од типот O–H···O and C–H···O.

Покрај определување на нивните кристални структури, пресметани се и геометриските параметри со помош на теоријата за функционал на електронската густина (B3LYP), користејќи базисни сетови 6-31G за асиметричните единки во комлексите. Пресметаните геометриски

[†] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

параметри се споредени со соодветните податоци добиени со рендгенска дифракција. Конструирани се, исто така, и мапи на електростатските потенцијали, а направени се и пресметки за молекулските орбитали за синтетизираните комплекси. Споредени се и експерименталните резултати од изучувањата на инфрацрвените спектри со оние добиени по теоретски пат.

Клучни зборови: ацесулфаматолиганд; бариум(II)-комплекс; стронциум(II)-комплекс; теоријата за функционал на електронската густина

1. INTRODUCTION

Acesulfame is a non-nutritive sweetener and is consumed since 1988, the year it was discovered. It is not digested or accumulated or changed in the human metabolism and is quickly excreted from the body [1]. While some ammonium-acesulfame compounds display acute oral toxicities, deterrent activity and skin irritation [2], choline acesulfamate is known having low toxicity [3]. In addition to biological importance of acesulfame, its coordination properties are important because acesulfame has potential donor atoms forming coordination bonds with metal ions [4].

In recent years, metal-organic frameworks (MOFs) or coordination polymers have attracted much attention because of their topology and potential applications in catalysis, absorption (gas storage), separation, luminescence, magnetism and drug delivery abilities [5–12].

The chemistry of the s-block elements is very interesting and they are preferred to transition or lanthanide metal ions, because s-block ions are generally non-toxic, inexpensive and soluble in aqueous media [5, 6]. Barium, being an s–block element, does not exist in nature in its elemental form, but it is present as divalent cations in combination with other elements [16]. Barium sulfate, which is an insoluble salt, is used as an enteric contrast agent for magnetic resonance studies [14, 15]. Strontium is also an alkaline earth metal, which in nature appears mainly as $SrSO_4$ or $SrCO_3$ [13]. Both, $BaSO_4$ and $SrSO_4$, exist also as biominerals in some marine species [16]. Besides, low doses of stable strontium have beneficial effect for treatment of osteoporosis [17–18]. In this paper properties of barium(II) and strontium(II) acesulfamate complexes forming 1D coordination polymers, are reported.

1.1. *General methods*

The IR spectra of the title compounds were recorded between 4000 – 400 cm^{-1} with a Bruker

Vertex 80V FT-IR spectrometer using KBr pellets. Single-crystal X-ray data were collected on a Stoe IPDS II [19] single crystal diffractometer employing monochromated MoKα radiation at 296 K. X-AREA [19] and X-RED [19] programs were used to cell refinement and data reduction respectively. SHELXS-97 [20] and SHELXL-97 [20] programs were used to solve and refine the structures respectively. ORTEP-3 for Windows [21] and Mercury [22] were used to prepare the figures. WinGX [23] and PLATON [24] software were used to prepare material for publication.

H9A and H9B atoms, given in Section 3, belong to both barium(II) and strontium(II) complexes and are located in a difference map and refined isotropically, but O9—H9A and O9—H9B bond distances were restrained as 0.82 (1) Å for the strontium(II) complex. The other H atoms attached to C atoms were positioned geometrically [C—H=0.930 Å and 0.960 Å] and refined using a riding model $U_{iso}(H)=1.2U_{eq}(C)$ and $1.5U_{eq}(C)$.

1.2. *Synthesis*

A 50 ml of hot aqueous solution (60 ℃) of acesulfame potassium salt (0.04 mol, 8.05 g) was gradually added to a 50 ml of hot stirred solution of barium perchlorate ($Ba(ClO_4)_2$) (0.02 mol, 6.72 g). The mixture was further stirred on a hot plate at 70 ℃ up to dryness. The formed complex separated from the resulting precipitate by absolute ethanol extraction where $KClO_4$ is not soluble. The final ethanolic solution was allowed to evaporate at room temperature for a few days and the x-ray quality crystals of compound 1 were obtained (yield 87%).

For compound 2, the procedure was exactly the same except a 50 ml of strontium perchlorate ($Sr(ClO_4)_2$) (0.02 mol, 5.73 g) solution was used. The x-ray quality crystals of compound 2 were obtained with the same procedure used for compound 1.

The crystal data of the complexes are given in Table 1.

T a b l e 1

Crystal data and structure refinement

Formula	[Ba(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]	[Sr(C$_4$H$_4$NO$_4$S)$_2$(H$_2$O)]
Crystal system	Monoclinic	Monoclinic
Color / shape	Colorless / Block	Colorless / Prism
Temperature	296 K	296 K
Space group	P12$_1$/c1	P12$_1$/c1
Unit cell dimensions		
	a = 8.2223 (3) Å	a = 7.9784 (5) Å
	b = 18.9945 (6) Å	b = 18.6171 (8) Å
	c = 11.7819 (4) Å	c = 11.5494 (7) Å
	β = 123.902 (2)º	β = 123.423 (4)º
Volume	1527.25 (9) Å^3	1431.79 (45) Å^3
Z	4	4
Density (calculated)	2.086 Mg m^{-3}	1.99 Mg m^{-3}
Wavelength	0.71073 Å	0.71073 Å
Reflections collected	21747	9025
Independent reflections	3006	2809
Absorption coefficient (μ)	2.92 mm^{-1}	4.11 mm^{-1}
Crystal size (mm)	0.470×0.350×0.240	0.780×0.487×0.270
Absorption correction	Integration X-RED	Integration X-RED
Data / parameters	3006 / 209	2809 / 209
Goodness-of-fit on F^2	1.1240	1.0580
θ ranges / (º)	2.08–27.31	2.11–27.29
h / k / l	−10, 10 / −23, 23 / −14, 14	−9, 9 / −22, 22 / −14, 13
Final R indices [I>2σ(I)]	R_1 = 0.023, wR_2 = 0.054	R_1 = 0.036, wR_2 = 0.091
Largest diff. peak and hole	0.41 e.Å^{-3}, −0.79 e.Å^{-3}	0.58 e.Å^{-3}, −0.61 e.Å^{-3}

2. THEORETICAL STUDY

Geometrical parameters were calculated by using the Gaussian 03 program package [25] and B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) approach in conjunction with the 6–31G(d,p) basis set. Initial values for the modeling were obtained from the x-ray data.

For the harmonic vibrational frequencies, the same process given above was used for finding the optimized structure. The obtained frequencies were scaled by 0.9627 [26]. The vibrational bands were assigned by using the Gauss-View molecular visualization program [27].

The molecular electrostatic potential $V(r)$, at a given point $r(x,y,z)$, in the vicinity of a molecule is defined in terms of the interaction energy between the electrical charge generated by the molecule's electrons and nuclei and a positive test charge (a proton) located at r. The $V(r)$ values were calculated for the system studied as described previously using the Equation 1 [28],

$$V(r) = \sum_{A} \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr', \qquad (1)$$

where Z_A is the charge of nucleus A located at R_A, $\rho(r')$ is the electronic density function of the molecule and r' is the dummy integration variable.

3. RESULTS AND DISCUSSION

3.1. *Crystallographic results*

Poly[octa-μ_3-acesulfamato-*O,O:N,O';O',N:O, O*-tetraaquatetrabarium(II)] and poly[octa-μ_3-ace-sulfamato-*O,O:N,O';O',N:O,O*-tetraaquatetrastronti-um(II)] complexes crystalize in centrosymmetric monoclinic space group P12$_1$/c1. The crystal structures are 1D coordination polymers and can be formulated as [Ba(acs)$_2$H$_2$O]$_n$ and [Sr(acs)$_2$H$_2$O]$_n$ (acs = acesulfame). In the literature, only 2D coordination polymer of acesulfame has been reported so far [29]. In the crystal structure, barium(II) and strontium(II) ions, which lie along *a*-axis and link acesulfamato ligands and barium(II) or strontium(II) ions, are bonded to two N-, four O$_{carbonyl}$-, two O$_{sulfonyl}$-atoms of acesulfamato ligands and one O-atom of aqua ligand. The crystal structures have two barium(II) and two strontium(II) centers along the *a*-axis and 1D polymer chains lay along the *a*-

axis. The two crystal structures are similar with the exception of metal ions. The Ba···Ba distances along the *a*-axis were found as 4.466 Å, and 4.473 Å and Sr···Sr distances were found as 4.289 Å and 4.334 Å. As can be seen in Figure 1, metal ions bond to two different acesulfamato ligands in asymmetric unit and the bond distances for these acesulfamato ligands are close to each other. Additionally, the dihedral angles between these acesulfamato ligands are 0.64 (17)° for barium(II) complex and 0.61 (18)° for strontium(II) complex. The theoretical values of these angles were found 64.62° for barium(II) complex and 76.03° for strontium(II) complex.
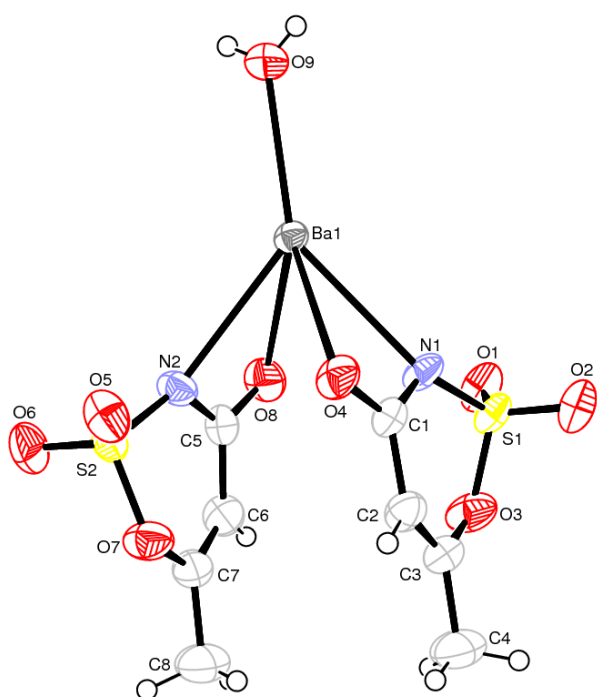
Fig. 1. The asymmetric unit of the barium(II) complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

The S—O bond distances of the barium(II) and strontium(II) complexes were found to be 1.429 (2) Å and 1.432 (3) Å for O1—S1; 1.424 (2) Å and 1.427 (2) Å for O5—S2; 1.415 (2) Å and 1.417 (3) Å for O2—S1; 1.414 (2) Å and 1.423 (3) Å for O6—S2; 1.611 (3) Å and 1.610 (3) Å for O3—S1; 1.613 (2) Å and 1.614 (3) Å for O7—S2, respectively. If the carbonyl groups are considered, C1—O4 and C5—O8 are 1.256 (3) Å and 1.253 (4) Å for barium(II) complex, 1.256 (4) Å and 1.245 (4) Å for strontium(II) complex, respectively. Some C—O bond distances for crystal structures which contain acesulfamate have been

reported for $[Cu(C_4H_4NO_4S)_2(C_6H_{14}N_2)_2]$ and $[Zn(C_6H_{14}N_2)_2(H_2O)_2](C_4H_4NO_4S)_2 \cdot 2H_2O$ [30] [e.g. C7—O3 and C7—O5 are 1.239 (3) Å and 1.251 (3) Å], for $[Ni(acs)_2(H_2O)_4]$ [4] [e.g. C1—O1 is 1.258(2) Å], for $[Cd_2(C_4H_4NO_4S)_2(C_6H_7N)_2]$ [31] [e.g. C13—O4 and C17—O5 are 1.244 (4) Å and 1.254 (3) Å], for $[Cu(C_4H_4NO_4S)_2(C_4H_5N_3)_2]$ [32] [e.g. C1—O1 is 1.274 (2) Å], for $[Co(C_4H_4NO_4S)_2(H_2O)_4]$ [33] [e.g. C1—O1 is 1.251 (3) Å], for $[K_2[PtCl_2L_2]$ [34] [e.g. C1—O4 is 1.221 (5) Å], for $K_2[PtCl_2(ace)_2]$ [35] [e.g. C1—O2 is 1.219 (5) Å], for $[Ca_2(acs)_2(H_2O)_2(acs)_2]_n$ [29] [e.g. C4—O7 is 1.255 (2) Å]. In the molecules, Ba—O and Sr—O bond distances are 2.750 (3) Å and 2.616 (3) Å for the aqua ligand; 2.927 (2) Å, 2.976 (2) Å and 2.819 (3) Å, 2.906 (3) Å for the carboxylate, respectively. Ba1—N1 and Ba1—N2 bond distances are 2.928 (2) Å and 2.949 (2) Å, respectively. Sr1—N1 and Sr1—N2 bond distances are 2.760 (3) Å and 2.770 (3) Å, respectively. As can be seen in Table 3, the bond distances between strontium and other atoms are not as long as bond distances between barium and other atoms. Since the electronic radius of the strontium is less than the electronic radius of the barium, this situation is predictable. The bond distances between Ba(II) ion and other atoms are 2.745 (2) Å for Ba1—O1[ii] [(ii) −*x*, −*y*, −*z*+1)], 2.6788 (19) Å for Ba1—O4[i] [(i) −*x*+1, −*y*, −*z*+1], 2.759 (2) Å for Ba1—O5[i] [(i) −*x*+1, −*y*, −*z*+1], 2.682 (2) Å for Ba1—O8[ii] [(ii) −*x*, −*y*, −*z*+1)]. Similarly, the bond distances between strontium(II) and other atoms are 2.581 (3) for Sr1—O1[i] [(i) −*x*, −*y*+1, −*z*], 2.513 (2) for Sr1—O4[ii] [(ii) −*x*+1, −*y*+1, −*z*], 2.586 (2) for Sr1—O5[ii] [(ii) −*x*+1, −*y*+1, −*z*], 2.508 (2) for Sr1—O8[i] [(i) −*x*, −*y*+1, −*z*].

1D polymeric chain structures of the complexes can be seen in Figure 2. In the molecule, barium(II) and strontium(II) ions, which bonded in the same way, have the coordination number of nine.

The crystal structure of barium(II) complex has O9—H9*A*···O6, O9—H9*B*···O2 and C8—H8*B*···O5 hydrogen bonds between chains, which extend along [100] direction and the geometric parameters belong to these hydrogen bonds are given in Table 2a. Similarly, the strontium(II) complex has the same hydrogen bonds with barium(II) complex and these hydrogen bonds present in the same part of the molecules. Moreover, the crystal structure of the strontium(II) complex has also C2—H2···O2 hydrogen bond. The detailed geometric parameters of these hydrogen bonds are given in Table 2b.
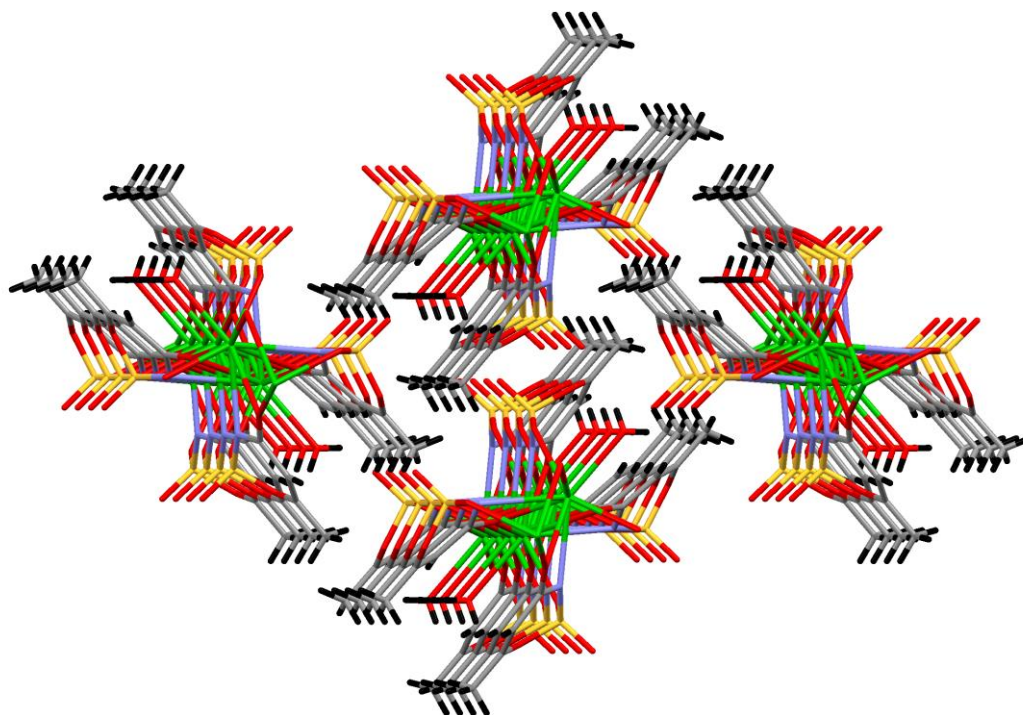
Fig. 2. 1D chain structure of the barium(II) complex

T a b l e 2a

Hydrogen-bond geometry for barium(II) complex (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$A\cdots$O6[i]	0.73 (6)	2.20 (6)	2.851 (4)	150 (6)
O9—H9$B\cdots$O2[ii]	0.72 (5)	2.23 (5)	2.916 (4)	159 (5)
C8—H8$A\cdots$O5[iii]	0.96	2.48	3.379 (5)	155

Symmetry codes: (i) $-x+1$, $y+1/2$, $-z+3/2$; (ii) $x+1$, y, $z+1$; (iii) $x-1$, $-y-1/2$, $z-1/2$.

T a b l e 2b

Hydrogen-bond geometry for strontium(II) complex (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$A\cdots$O6[i]	0.82 (1)	2.23 (4)	2.925 (4)	143 (6)
O9—H9$B\cdots$O2[ii]	0.82 (1)	2.34 (4)	3.034 (4)	143 (6)
C8—H8$A\cdots$O5[iv]	0.96	2.42	3.287 (5)	150
C2—H2$\cdots$O2[iii]	0.93	2.42	3.287 (5)	150

Symmetry codes: (i) $-x+1$, $y-1/2$, $-z+1/2$; (ii) $x+1$, y, $z+1$; (iii) $-x$, $-y+1$, $-z-1$; (iv) $x-1$, $-y+3/2$, $z-1/2$.

3.2. *Theoretical results*

The obtained theoretical value of C3—O3 bond distance for barium(II) complex is closer to the experimental value than the other bond distances and both experimental and calculated values of this bond are 1.386 (4) Å and 1.3841 Å, respectively. The least difference between theoretical and experimental values for strontium(II) complex was obtained for C1—C2 bond distance with 0.0002 Å difference. The biggest difference between experimental and theoretical values for both compound 1 and compound 2 was found in O3—S1 bond. The experimental and theoretical values for this bond distance are 1.611 (3) Å, 1.9061 Å for compound 1 and 1.610 (3) Å, 1.9057 Å for compound 2, respectively. When the experimental and theoretical bond distances were compared, theoretical values are more inconsistent with the experimental values for the O—S bonds than the other bond distances. The experimental and theoretical bond distances of complexes are given in Table 3.

T a b l e 3

*Some selected bond distances of the barium(II) and strontium(II) complexes (Å) (**M**=Ba (II), Sr (II)).*

	Compound 1		Compound 2	
Atoms	**X-ray**	**B3LYP/6-31G(d,p)**	**X-ray**	**B3LYP/6-31G(d,p)**
C1—C2	1.450 (4)	1.4561	1.453 (5)	1.4528
C5—C6	1.453 (4)	1.4562	1.455 (5)	1.4528
C2—C3	1.325 (4)	1.3686	1.329 (5)	1.369
C6—C7	1.317 (5)	1.3686	1.323 (5)	1.369
C3—C4	1.483 (5)	1.5049	1.474 (5)	1.5047
C7—C8	1.486 (5)	1.5048	1.482 (5)	1.5047
C1—N1	1.349 (4)	1.3941	1.347 (4)	1.3929
C5—N2	1.353 (3)	1.3941	1.356 (4)	1.393
C1—O4	1.256 (3)	1.2917	1.256 (4)	1.2942
C5—O8	1.253 (4)	1.2916	1.245 (4)	1.2942
C3—O3	1.386 (4)	1.3841	1.391 (4)	1.3834
C7—O7	1.381 (4)	1.3844	1.389 (4)	1.3834
N1—S1	1.567 (2)	1.7423	1.571 (3)	1.7419
N2—S2	1.555 (2)	1.7419	1.565 (3)	1.7421
O1—S1	1.429 (2)	1.6201	1.432 (3)	1.6212
O5—S2	1.424 (2)	1.6054	1.427 (2)	1.6036
O2—S1	1.415 (2)	1.6052	1.417 (3)	1.6036
O6—S2	1.414 (2)	1.6198	1.423 (3)	1.6212
O3—S1	1.611 (3)	1.9061	1.610 (3)	1.9057
O7—S2	1.613 (2)	1.9062	1.614 (3)	1.9056
M—N1	2.928 (2)	2.8037	2.760 (3)	2.6278
M—N2	2.949 (2)	2.8021	2.770 (3)	2.6284
M—O4	2.927 (2)	2.8133	2.819 (3)	2.6173
M—O8	2.976 (2)	2.8154	2.906 (3)	2.6166
M—O9	2.750 (3)	2.6501	2.616 (3)	2.4847

The smallest value between experimental and theoretical bond angles was found as 0.3226° for C7—O7—S2 of barium(II) complex and as 1.6105° for C3—O3—S1 of strontium(II) complex. The calculated bond angles for compound 1 are more consistent than the calculated angles for compound 2 compared to the experimental angles.

The experimental and theoretical values for the first complex are 115.95 (15)°, 117.5039° for O1—S1—O2 and 116.01 (15)°, 117.5272° for O5—S2—O6, respectively. Some selected experimental and theoretical bond angles of the barium(II) and strontium(II) complexes can be seen in Table 4.

T a b l e 4

*Some selected bond angle of the barium(II) and strontium(II) complexes (°) (**M** = Ba(II), Sr(II)).*

	Compound 1		Compound 2	
Atoms	**X-ray**	**B3LYP/6-31G(d,p)**	**X-ray**	**B3LYP/6-31G(d,p)**
C1—C2—C3	122.6 (3)	125.2674	122.6 (3)	124.9555
C5—C6—C7	122.6 (3)	125.2147	122.8 (3)	124.971
C2—C3—C4	127.7 (3)	124.791	128.1 (4)	124.7951
C6—C7—C8	128.6 (3)	124.792	129.0 (3)	124.7937
C1—N1—S1	119.8 (2)	121.7316	119.5 (2)	121.9907
C5—N2—S2	120.1 (2)	121.6982	119.7 (2)	121.9731
C3—O3—S1	117.4 (2)	118.4888	117.5 (2)	119.1105
C7—O7—S2	118.0 (2)	118.3226	117.5 (2)	119.1366
N1—C1—O4	118.4 (3)	113.4065	117.8 (3)	112.7855
N2—C5—O8	118.0 (3)	113.4084	117.6 (3)	112.7872
N1—**M**—O4	44.92 (6)	47.1285	47.10 (7)	50.5309
N2—**M**—O8	44.29 (6)	47.1211	46.07 (7)	50.5337
N1—S1—O3	106.07 (13)	103.5283	105.86 (14)	103.3259
N2—S2—O7	106.63 (13)	103.3944	106.36 (14)	103.3556
O1—S1—O2	115.95 (15)	117.5039	116.01 (15)	117.6775
O5—S2—O6	115.63 (15)	117.5272	115.63 (16)	117.6724

When the torsional angles are considered, the nearest theoretical and experimental values for barium(II) and strontium(II) complexes should be found for C1—C2—C3—O3 and O4—C1—N1—S1. Because the theoretical values were calculated for asymmetric unit, the reason of the large differences between experimental and theoretical values for torsional angles seems to be interesting and needs to be determined. Some torsional angles of compounds are given in Table 5.

T a b l e 5

*Some selected torsion angle of the barium(II) and strontium(II) complexes (°) (**M** = Ba(II), Sr(II)).*

Atoms	Compound 1		Compound 2	
	X-Ray	B3LYP/6-31G(d,p)	X-Ray	B3LYP/6-31G(d,p)
C1—C2—C3—C4	−175.6 (4)	177.2496	175.5 (4)	−177.7162
C5—C6—C7—C8	−168.7 (4)	176.9455	167.8 (4)	−177.789
C1—C2—C3—O3	1.8 (5)	−1.3874	−3.0 (6)	0.9809
C5—C6—C7—O7	5.3 (5)	−1.5797	−6.7 (6)	0.9363
C1—N1—S1—O3	34.4 (3)	−8.161	−34.9 (3)	3.1217
C5—N2—S2—O7	32.9 (3)	−9.9324	−35.1 (3)	2.6503
O4—**M**—N1—C1	11.07 (16)	−8.681	−10.70 (18)	8.723
O8—**M**—N2—C5	12.89 (16)	−8.5886	−12.76 (17)	8.7646
O4—C1—N1—S1	171.2 (2)	175.6317	−172.0 (3)	−172.3077
O8—C5—N2—S2	172.6 (2)	176.3187	−172.7 (3)	−172.1311

3.3. *Frontier molecular orbital*

The HOMO-1, HOMO, LUMO and LUMO+1 orbitals were calculated for asymmetric units of barium(II) complex and the distributions and energy levels of these orbitals are presented in Figure 3. As can be seen in Figure 3, LUMO+1, LUMO, HOMO and HOMO−1 frontier molecular orbitals of the barium(II) complex are distributed on whole surface of the molecule. While the LUMO+1 and LUMO orbitals display similar distribution, the HOMO and HOMO−1 display similar distribution on molecule.

The electrons are not delocalized on Ba1 atom in all molecular orbitals, whereas the barium(II) is not coordinated fully. Additionally, although the LUMO+1 and LUMO orbitals are localized on O9 atom, HOMO and HOMO−1 orbitals are not localized on O9 atom. If the HOMO-LUMO gap is considered, the energy difference between HOMO and LUMO is 4.0727 eV.

The LUMO+1, LUMO, HOMO and HOMO−1 orbitals of the strontium complex are also distributed on all surface of the molecule similar to the barium(II) complex. The HOMO-LUMO gap energy value for this molecule was calculated as 4.0504 eV. The HOMO-LUMU gap energies both barium(II) and strontium(II) complexes are almost at the same level.
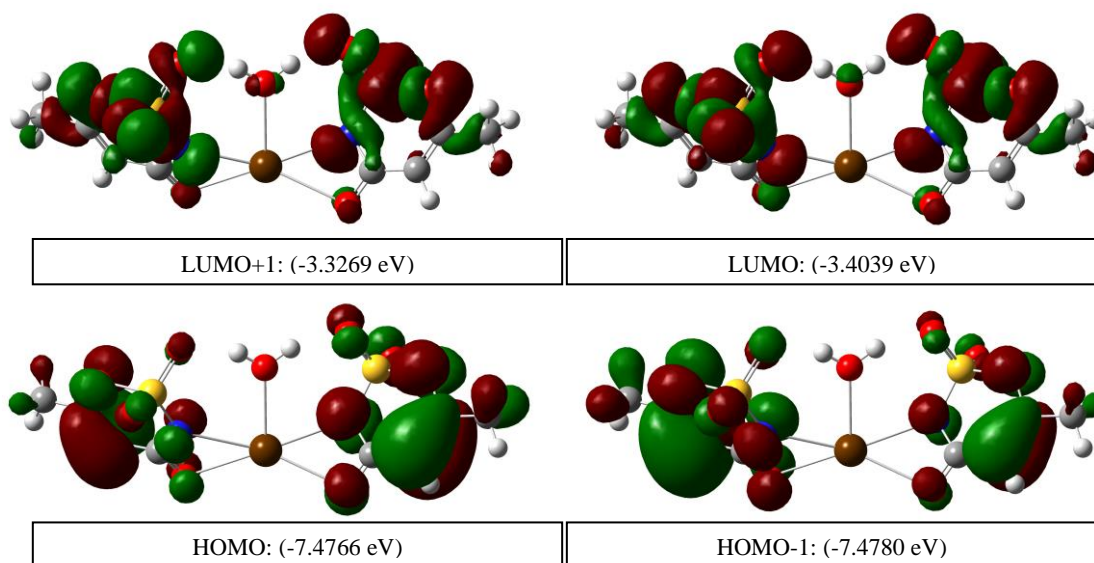

LUMO+1: (-3.3269 eV)	LUMO: (-3.4039 eV)
HOMO: (-7.4766 eV)	HOMO-1: (-7.4780 eV)

Fig. 3 Molecular orbital surfaces and energy levels are given for HOMO-1, HOMO, LUMO and LUMO+1 of the title compound (1) computed at the B3LYP/6-31G(d,p)

3.4. *Molecular electrostatic potential (MEP)*

We used MEP values that correspond to the surface determined from points with electronic density ρ 0.0004 a.u. The molecular electrostatic potential map of barium(II) complex is given in the Figure 4. The most positive region with 0.1340 a.u. is the environment of barium(II) ion, which is not coordinated fully. The most negative regions are in the vicinity of the O1, O2, O5 and O6 atoms. The O9—H9A···O6, O9—H9B···O2 and C8—H8B···O5 hydrogen bonds exist in the crystal structure of the barium(II) complex and this result is consistent with theoretical study.
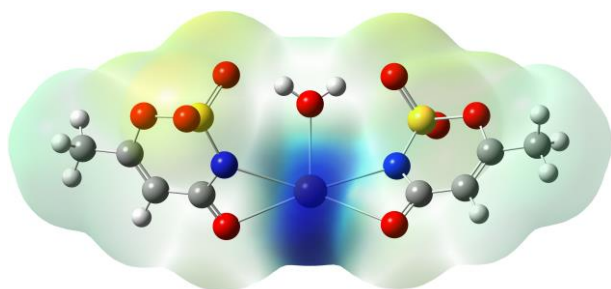
Fig. 4. Molecular electrostatic potential map of asymmetric unit calculated for barium(II) complex at the B3LYP/6-31G(d,p) level

When the strontium(II) complex is considered, the most positive region can be seen as surrounding the strontium atom with 0.139 a.u. The most negative regions are around of O1, O2, O5 and O6 atoms similar to barium(II) complex almost with –0.0435 a.u., –0.045 a.u., –0.0455 a.u. and –0.0278 a.u., respectively.

3.5. *Vibrational spectrum*

The experimental spectra of barium(II) and strontium(II) complexes were also compared with the theoretical spectra of those complexes in 4000-600 cm^{-1} ranges.

The experimental and theoretical spectra that belong to barium(II) and strontium(II) complexes can be seen in Figure 5a and Figure 5b. The experimental stretching vibrations that belong to aqua ligand are being observed at around 3527 cm^{-1} and 3590 cm^{-1} for barium(II) complex and at around 3625 cm^{-1} and 3554 cm^{-1} for strontium(II) complex. The theoretical asymmetric stretching vibrations of O—H for barium(II) and strontium(II) complexes were calculated at around 3480.16 cm^{-1} and 3474.98 cm^{-1}, respectively, and the most strong vibrations of the O—H were observed at these frequencies.

While the experimental asymmetric SO$_2$ and symmetric SO$_2$ stretching frequencies were observed at 1329 cm^{-1} and 1172 cm^{-1} for compound 1 and at 1330 cm^{-1} and 1179 cm^{-1} for compound 2, the experimental C=O stretching vibrations were observed at 1652 cm^{-1} for compound 1 and at 1647 cm^{-1} for compound 2. Some experimental and theoretical stretching frequencies belonging to the compounds under study are given in Table 6.
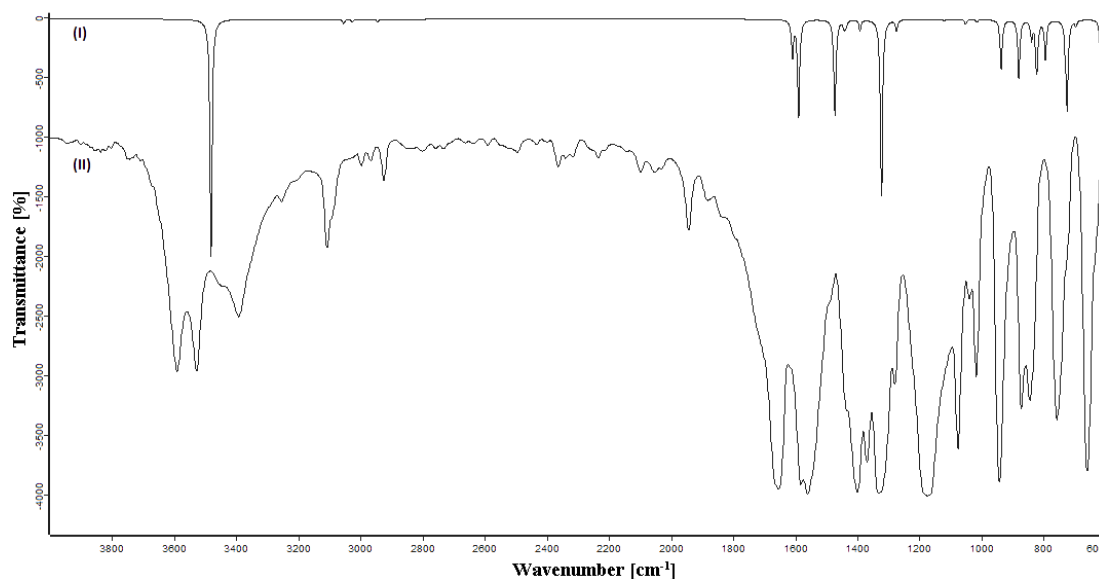
Fig. 5a. Theoretical IR spectrum of the compound 1 with (I), experimental IR spectrum of the title compound with (II) in 4000–600 cm^{-1} ranges
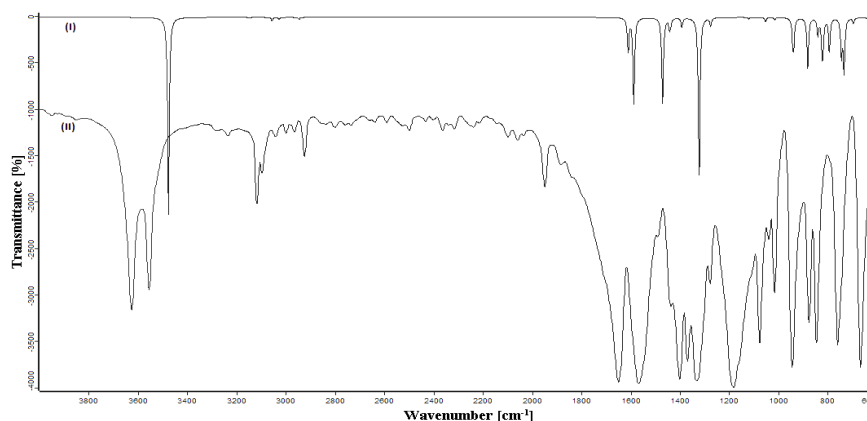
Fig. 5b. Theoretical IR spectrum of the compound 2 with (I), experimental IR spectrum of the title compound with (II) in 4000-600 cm^{-1} ranges.

T a b l e 6

Some vibrational frequencies of the barium(II) and strontium(II) complexes (cm^{-1}).

	Compound 1		Compound 2	
Assignments	**Experimental**	**B3LYP/6-31G(d,p)**	**Experimental**	**B3LYP/6-31G(d,p)**
ν(O—H)	3527, 3590	3480.16, 3363.71	3625, 3554	3474.98, 3360.76
ν(C=O)	1652	1471.05, 1468.98	1647	1469.6, 1467.43
ν(C=C)	1579	1587.27, 1585.98	1565	1585.48, 1584.12
ν_{as}(SO$_2$)	1329	934.477, 932.459	1330	935.684, 933.247
ν_s(SO$_2$)	1172	820.659, 817.171	1179	819.579, 815.534

Appendix A. Supplementary Data

CCDC 873867 (1) and CCDC 873863 (2) contain the supplementary crystallographic data for this report. This data can be obtained free of charge via https://www.ccdc.cam.ac.uk/ services/structure_deposit/ or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

4. CONCLUSION

The crystal structures of two one-dimensional coordination polymers were investigated by X-ray diffraction technique and the molecular properties calculated by DFT methods with B3LYP/6-31G(d,p) basis set. Both barium(II) and strontium(II) complexes have the coordination number of nine and show similar crystal structure. In each complex, one aqua ligand and two acesulfamato ligands are coordinated to barium(II) and strontium(II) ions. The hydrogen bonds between the chains present in the crystal structure and these hydrogen bonds establish three-dimensional networks. The energy gap of HOMO-LUMO found to be 4.0727 eV for barium(II) complex and 4.0504 eV for strontium(II) complex with B3LYP/6-31G(d,p). These energy differences almost are the same level. As shown at MEP, while the electro-

philic attach centers of this complex are at the environment of sulfonyl oxygen and the intermolecular hydrogen bonds are shown at these regions from information obtained by x-ray diffraction.

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