

Synthesis and Quantumchemical Study on $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ Complexes

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Abstract Using hydrothermal synthesis $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ complexes were obtained, which were characterized by X-ray and thermo-gravimetric analysis. The geometric and electronic structure parameters were calculated with the Density Functional Theory at the B3LYP level with 6-31G(d) basis set for H, O, S, Se and LANL2DZ for Hf in gas phase. The bond orders of the complexes were determined. HOMO-LUMO energies and calculated structures are shown. The key role in the LUMO play the *d*-atomic orbitals of Hf(IV). The data obtained for the selenate are reported for a first time.

Keywords Hydrothermal synthesis, X-ray analysis, Density functional theory, Geometry optimization

1. Introduction

The elements of zirconium and hafnium form mixed crystals in nature because of their analogical chemical properties of their atoms. During decades different methods and technologies were developed for their separation with an aim to obtain hafnium which possesses the ability to absorb neutrons. This property occurs to be very useful for regulation of nuclear reactions [1, 2]. For the syntheses of different more complicated compounds of hafnium of certain interest are its simple salts because of the chemical sustainability of hafnium and its oxide HfO_2 . Different hafnium sulfates, which are isomorphous with the corresponding zirconium once, have been obtained by a reaction between HfO_2 and sulfuric acid with concentrations in the range 50–90% and continuous evaporation of the solutions [3]. Their thermal stability was investigated and the intermediated products of destruction were defined. In general, the data concerning the structure and properties of the hafnium sulfates are scarce and not enough systematized [4-6]. Moreover, no data in the literature is found about the obtainment and characterization of hafnium selenites, salanates, and tellurates. The obtaining and the structure of $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ [7] is reported only. Having in mind, the isostructure of the zirconium sulfate with this of hafnium, it can be expected that hafnium selenate may have analogical symmetry and similar crystalline-chemical characteristic with these of zirconium selenate.

2. Materials and Computational Methods

Hafnium sulfate and hafnium selenate with a chemical composition $\text{Hf}(\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$ (X = S, Se) were obtained using the method of hydrothermal synthesis. The hydrothermal synthesis was carried out in a metal-teflonic autoclave with capacity 20 cm³ at 300°C for 6 hours as to 1 g HfO_2 (Merck), 5 cm³ 96-98% H_2SO_4 (Merck) and H_2SeO_4 (Merck) were added correspondingly. After the synthesis was over, the solid phase was washed with ethanol and dried at 100°C.

The symmetry and the crystallographic parameters of the initial hafnium oxide, as well as the characterization of the obtained hafnium sulfate and selenate was determined using powder diffraction and thermal analyses. On the base of these analyses it is evident that the obtained substances are $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$.

The quantum chemical calculations of the obtained compounds and HfO_2 were realized by Becke's three-parameter hybrid functional, combined with the Lee-Yang-Parr – B3LYP [8] correlation function from the density functional theory basis set with added polarization functions of H, S, Se и O – 6-31G(d) and LANL2DZ for Hf, with the help of Gaussian03 [9]. Convergence criterion 10⁻⁸ a.u. for all calculations was used. The normal vibrations for each optimized molecule were calculated in order to investigate the nature of the reached stationary point in the optimization procedure. No imaginary frequencies for the structures were found, which means that they correspond to a status of minimum potential energy.

To prepare the calculations and visualization of the results

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HyperChem 5.0 [10] and Molekel 5.4 program products [11] were used.

3. Results and Discussion

The symmetry and the crystallographic parameters of the initial hafnium oxide, as well as the characterization of the obtained hafnium sulfate and selenate was determined using X-ray analysis [12]. The data obtained are shown in Fig. 1.

The powder X-ray analysis shows that the used for hydrothermal synthesis hafnium dioxide possesses monoclinic symmetry (group $P2_1/C$) and parameters of the elementary cell: $a = 5.1170\text{\AA}$, $b = 5.1754\text{\AA}$, $c = 5.2915\text{\AA}$ and $\alpha = \gamma = 90.00^\circ$, $\beta = 99.216^\circ$. The obtained hafnium sulfate is a tetrahydrate with a composition $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and the results prove orthorhombic symmetry (group $Fddd$) and parameters $a = 25.8700\text{\AA}$, $b = 5.5300\text{\AA}$, $c = 11.5900\text{\AA}$, $\alpha = \beta = \gamma = 90.00^\circ$. The data from analogical investigations by other authors [1, 2] fully coincide with those obtained by us, which is evidence that the hydrothermal synthesis gives a tetrahydrate product. This product is isostructural with $\text{Zr}(\text{SO}_4)_2(\text{H}_2\text{O})_4$.

There is no data in the literature about X-ray analysis of hafnium selenates. Crystallographic parameters for $\text{Zr}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ [7] are reported, which analogically with the sulfate should be isostructural with hafnium selenate.

The experimental data show, that the newly synthesized selenate is with composition $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$, possesses orthorhombic symmetry (group $Fddd$) and parameters of the elementary cell: $a = 26.4900\text{\AA}$, $b = 5.6558\text{\AA}$, $c = 11.9489\text{\AA}$, $\alpha = \beta = \gamma = 90.00^\circ$. These data are analogous with the one for zirconium selenate [7]. From Fig. 1 and the obtained experimental data for the symmetry and crystallographic parameters is evident that the obtained $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ are isostructural. From the roentgenograms can be seen that both samples of the sulfate and selenate register peaks corresponding to HfO_2 , which has not reacted. The molecules of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ и $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ are visualized in Figure 2. The numbering of the atoms is given also. The results from the geometric optimization of the two molecules are given in Table 1.

From the table can be seen that the values for the lengths of the bonds Hf–O and the angles O–Hf–O in the molecules of the two complexes are overlapping, while those for Se–O and O–Se–O are greater in comparison with those in the sulfur complex. It can be expected, that after dehydration of the complexes the waterless salt $\text{Hf}(\text{SeO}_4)_2$ will be thermally less stable than $\text{Hf}(\text{SO}_4)_2$.

The electrostatic potential was calculated in order to investigate the reaction properties of the molecules with the chosen method of calculation [13].

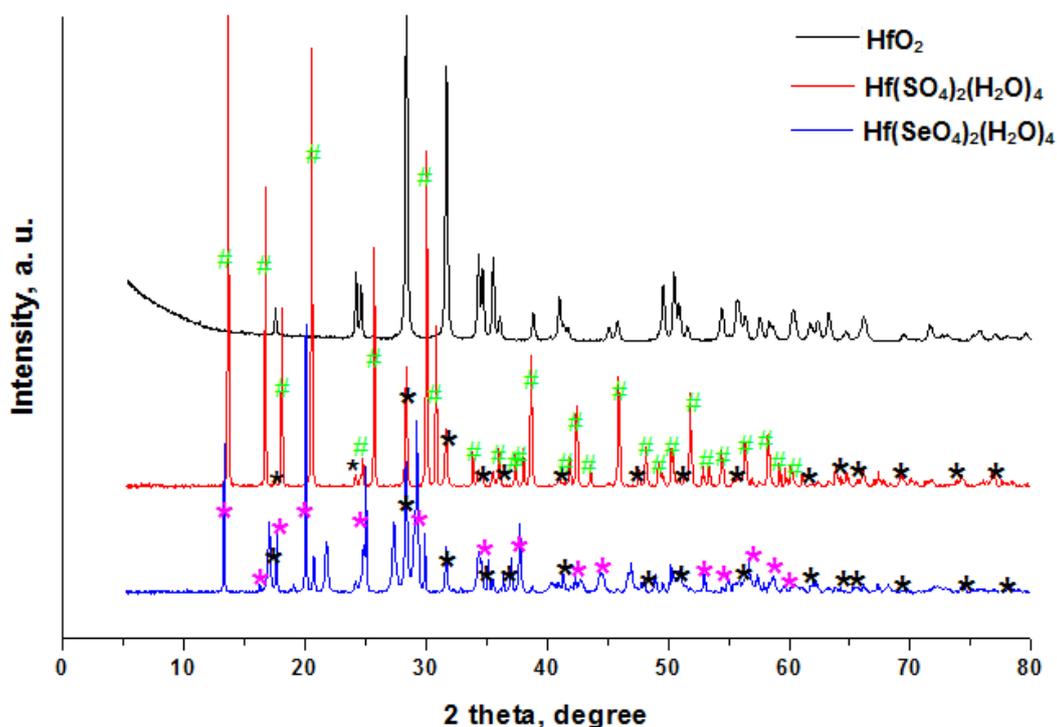
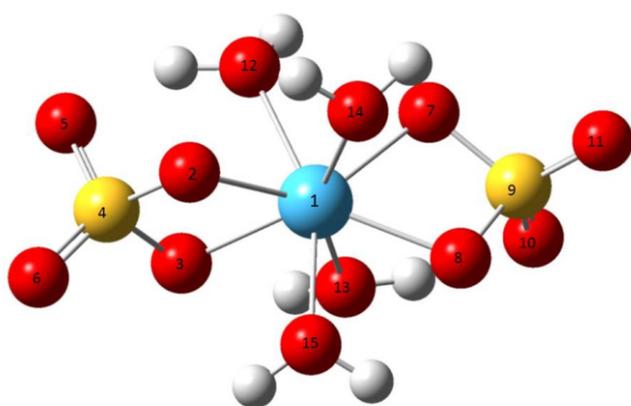


Figure 1. X-ray analysis of $\ast\text{-HfO}_2$, $\#\text{-Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\ast\text{-Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$

Table 1. Optimized geometrical parameters of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$

Parameters	Bond length (Å)		Parameters	Bond angle (grad)	
	$\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$	$\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$		$\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$	$\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$
$\text{Hf}-\text{O}^{2(8)}$	2.140	2.143	$\text{O}^{2(7)}-\text{Hf}-\text{O}^{3(8)}$	65.9	69.6
$\text{Hf}-\text{O}^{3(7)}$	2.139	2.160	$\text{O}^{3(2)}-\text{Hf}-\text{O}^{8(7)}$	133.9	130.6
$\text{S}(\text{Se})^{4(9)}-\text{O}^{2(8)}$	1.586	1.742	$\text{O}^{2(7)}-\text{S}(\text{Se})^{4(9)}-\text{O}^{3(8)}$	94.4	107.0
$\text{S}(\text{Se})^{4(9)}-\text{O}^{3(7)}$	1.587	1.741	$\text{O}^{5(10)}-\text{S}(\text{Se})^{4(9)}-\text{O}^{6(11)}$	118.4	119.8
$\text{S}(\text{Se})^{4(9)}-\text{O}^{5(10)}$	1.484	1.652	$\text{O}^{2(8)}-\text{Hf}-\text{O}^{12(13)}$	76.2	76.9
$\text{S}(\text{Se})^{4(9)}-\text{O}^{6(11)}$	1.451	1.616	$\text{O}^{7(3)}-\text{Hf}-\text{O}^{14(15)}$	79.5	76.3
$\text{Hf}-\text{O}^{12(13)}$	2.243	2.243	$\text{O}^{12(15)}-\text{Hf}-\text{O}^{14(13)}$	89.1	88.7
$\text{Hf}-\text{O}^{14(15)}$	2.262	2.279	$\text{O}^{14(12)}-\text{Hf}-\text{O}^{13(15)}$	154.7	153.3
			$\text{O}^{7(3)}-\text{Hf}-\text{S}(\text{Se})^{4(9)}-\text{O}^{6(11)}$	179.9	176.3
			$\text{O}^{5(6)}-\text{S}(\text{Se})^4-\text{S}(\text{Se})^9-\text{O}^{11(10)}$	88.7	90.2

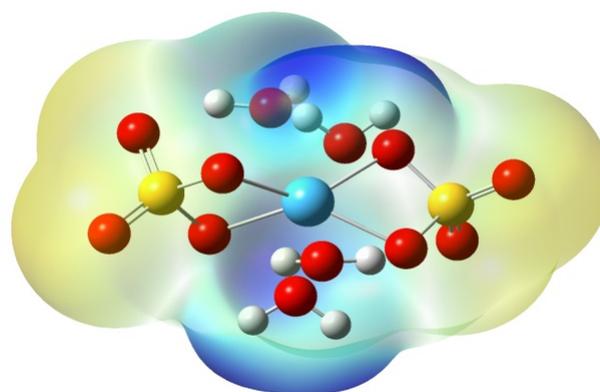
**Figure 2.** Optimized geometrical structure and atomic labeling of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ (O-atoms are in red, Hf-atom is blue, S(Se)-atoms are in yellow)

The electrostatic potential is a real physical property, reflecting the effect of the interaction between the nucleuses and the electrons in one molecule and can be determined experimentally by diffraction methods or calculated.

The computed molecular electrostatic potential of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ is presented in Figure 3. In yellow color are the negative values and in blue the positive. It was found, that the most negative value of the molecular electrostatic potential for $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ is -0.050 a.u., and the most positive 0.087 a.u. The same for $\text{Hf}(\text{SeO}_4)_2(\text{H}_2\text{O})_4$ are respectively -0.044 and 0.079 a.u.

Quantum-chemical calculations provide the ability to calculate the pure charges (q), which are localized at the corresponding atoms as a result of the redistribution of the electrons in the molecule. Though they are not connected with physical properties and cannot be observed experimentally, they allow the understanding of the distribution of the electronic density in a system of connected atoms and predict some chemical properties of the

molecules. The net atomic charges, calculated by Mulliken [14] and the order of the bonds in the investigated compounds are presented in Table 2.

**Figure 3.** Electrostatic potential on the surface of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$

The selenium atom localizes greater part of pure charge in its complex because of the less pronounced electro-negativity in comparison to the sulfur atom, which reflects on the distribution of the electronic density at the oxygen atoms.

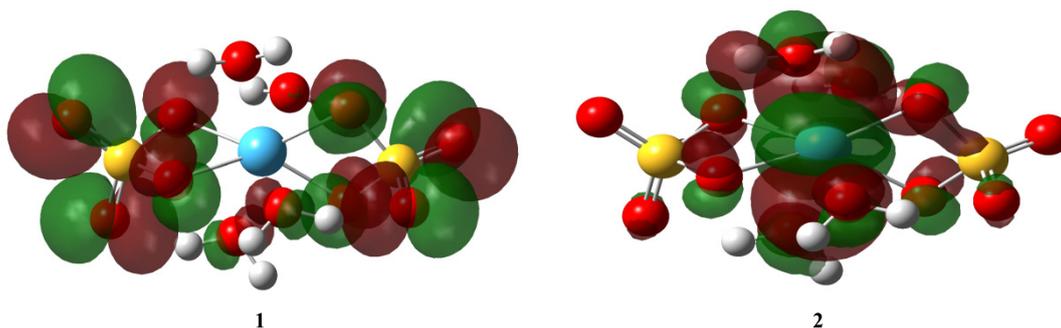
As a whole, the orders of the different bonds in the sulfur complex are lower from the analogous bonds in the selenium complex.

Homo- and Lumo-molecular orbitals (MO) of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ are visualized in Figure 4.

From Figure 4 can be seen that Homo MO of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ are combined mainly of oxygen atoms, while Lumo MO are composite of atomic orbitals of hafnium as the most significant is the contribution of the d -orbitals. More quantum-chemical data concerning the calculated energy, dipole moment of the molecules, the energies of Homo and Lumo orbitals and the difference between them for the investigated complexes are given in Table 3.

Table 2. Mulliken atomic charges and bond orders of Hf(SO₄)₂(H₂O)₄ and Hf(SeO₄)₂(H₂O)₄

Atom	Mulliken atomic charges		Bond	Bond order	
	Hf(SO ₄) ₂ (H ₂ O) ₄	Hf(SeO ₄) ₂ (H ₂ O) ₄		Hf(SO ₄) ₂ (H ₂ O) ₄	Hf(SeO ₄) ₂ (H ₂ O) ₄
Hf	1.388	1.499	Hf–O ²⁽⁸⁾	0.860	0.891
O ²⁽⁸⁾	–0.724	–0.712	Hf–O ³⁽⁷⁾	0.871	0.870
O ³⁽⁷⁾	–0.721	–0.710	S(Se) ⁴⁽⁹⁾ –O ²⁽⁸⁾	1.186	1.225
O ⁵⁽¹⁰⁾	–0.591	–0.621	S(Se) ⁴⁽⁹⁾ –O ³⁽⁷⁾	1.184	1.236
O ⁶⁽¹¹⁾	–0.487	–0.538	S(Se) ⁴⁽⁹⁾ –O ⁵⁽¹⁰⁾	1.699	1.741
O ¹²⁽¹³⁾	–0.817	–0.821	S(Se) ⁴⁽⁹⁾ –O ⁶⁽¹¹⁾	1.926	2.011
O ¹⁴⁽¹⁵⁾	–0.778	–0.770	Hf–O ¹²⁽¹³⁾	0.662	0.665
S(Se) ⁴⁽⁹⁾	1.486	1.503	Hf–O ¹⁴⁽¹⁵⁾	0.623	0.612



$$\Psi_{\text{Homo}} = -7.6\% 2p_y(\text{O}^{11}) + 7.6\% 2p_y(\text{O}^6) + 6.82\% 3p_y(\text{O}^{10}) - 6.82\% 2p_y(\text{O}^5) + 4.5\% 3p_y(\text{O}^6) - 4.5\% 3p_y(\text{O}^{11})$$

$$\Psi_{\text{Lumo}} = 69.1\% 7d_{z^2}(\text{Hf}) - 7.1\% 7d_{x^2-y^2}(\text{Hf}) - 4.8\% 7d_{xy}(\text{Hf}) + 3.5\% 8d_{z^2}(\text{Hf}) + 1.2\% 3s(\text{Hf}) + 1.2\% 2s(\text{Hf})$$

Figure 4. Homo MO – (1) and Lumo MO – (2) of Hf(SO₄)₂(H₂O)₄**Table 3.** Calculated electronic properties of Hf(SO₄)₂(H₂O)₄ and Hf(SeO₄)₂(H₂O)₄

Compound	E _{tot} (a.u.)	HOMO (a.u.)	LUMO (a.u.)	ΔE _{HOMO-LUMO} (a.u.)	μ (D)
Hf(SO ₄) ₂ (H ₂ O) ₄	–1752.9589	–0.29266	–0.05474	0.2379	0.6115
Hf(SeO ₄) ₂ (H ₂ O) ₄	–5754.3085	–0.30082	–0.05758	0.2432	1.0724

The data show that the calculated full energy for the molecule of hafnium selenate tetrahydrate is lower than this of the isostructural sulfate. The difference in the energies of Homo and Lumo orbitals is close for both of the compounds, while for the calculated dipole moment this difference is significant. The molecule of Hf(SeO₄)₂(H₂O)₄ possesses greater dipole moment in comparison to that of Hf(SO₄)₂(H₂O)₄. This fact may have importance for analyzing the behavior of the investigated compounds when dissolved in water or other solvents as well as for studying the opportunity for obtaining other hafnium compounds in solution.

4. Conclusions

Hafnium sulfate and hafnium selenate were synthesized using hydrothermal method. The substances were characterized by X-ray analysis and it was found that they

are tetrahydrates – Hf(SO₄)₂(H₂O)₄ and Hf(SeO₄)₂(H₂O)₄. The crystallographic symmetry and the parameters of the elementary cell of the obtained substances and the initial reagent HfO₂ were determined. The data for the sulfate totally coincide with the literature data and these for the hafnium selenate are reported for a first time. The geometry and the electronic structure, the net atomic charges according Mulliken and the order of the bonds in the obtained substances were calculated applying the density functional theory. The quantum chemical investigations are of certain interest for the chemistry of hafnium and its compounds which are not studied enough.

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