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The Development Of Research Competence Based On Quantum Calculation Of Molecular Systems

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ABSTRACT

The integration of instruction and research represents one of the fundamental goals of contemporary educational system. Elaborating effective mechanisms for applying research methods able to make science more attractive could solve the problem of motivating young people to study in this difficult but necessary field for society development. The study proposes a model of using chemical synthesis, studying molecular structure and composition of coordination compounds, applying quantum-chemical calculations and testing biological properties.

The set of applied methods allows for a detailed analysis of certain features related to the structure and properties of new chemical compounds and is recommended for application within university courses and at pre-university level- for interested students.

Keywords: research competences, innovation, pedagogical model, quantum calculations, interdisciplinarity.

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INTRODUCTION

One of the major tasks of contemporary pedagogy consists in developing effective mechanisms for harmonious integration of technologies within the accelerated development of field knowledge based on the forecasted needs of tomorrow's society citizen. The achievement of this task involves deep inter and trans disciplinary connections [1, 2]. It's obvious that Chemistry has the tightest bonds with Physics and Biology yet, due to the dynamical development of informational technologies and their implementation in different fields, including research and instruction, it appears the need to elaborate different strategies of developing students' competences of using ICT within the chemistry field [3].

The modern paradigm of university education requires an effective integration of instruction and research- process that would allow for a faster and easier transfer of new scientific findings within university curricula. Moreover, the students will graduate with solid competences based on the interconnection of knowledge-application-innovation domains.

The motivation for a quality and conscious instruction in the field of Natural and Exact sciences can be achieved only by means of some well analyzed algorithms, where instruction and research are indispensable and lead to the development of the research competence with the formation of innovative thinking elements [4-6]. Within chemistry, there can be proposed several models that would permit to achieve complex studies of molecular characteristics [7], and chemical processes, allowing pupils/ students to go through simple substances → the synthesis of complex systems – analysis of composition and structure based on chemical and physical methods → molecular energy calculation, determining the substitution and condensation possibilities in certain functional groups → determining the useful properties and the domains of practical application.

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In order to organize some profound studies, it is proposed the analysis of an instruction-research integrated application model, where the synthesis of coordination compounds is preceded by studies with the application of physical, informational and biological methods, so as to form in pupils/students competences of deep and complete analysis (experimental and chemical) of new chemical compounds. The Model bases on the application GAMESS program, that contains different calculation methods, starting with those of molecular mechanics and dynamics, semi-empirical methods, *ab initio* methods based on Hartree-Fock theory or methods based on the theory of density functional, and can be used for the calculation of a very wide range of molecular properties [8].

METHODS AND MATERIALS

The new coordination compounds of zinc with 1,2-cyclohexanedione dioxime: $[Zn(CH_3COO)_2(NioxH_2)(S\text{-}Nia)(H_2O)]\cdot DMF$ (**1**), $[Zn(CH_3COO)_2(NioxH_2)(DMF)(H_2O)]$ (**2**), $[Zn(CH_3COO)_2(NioxH_2)(Nia)(H_2O)]$ (**3**) and $[Zn(CH_3COO)_2(NioxH_2)(INia)(H_2O)]$ (**4**), where $NioxH_2$ - 1,2- cyclohexanedione dioxime, S-Nia – thio-nicotinamide, Nia – nicotinamide, INia – izo-nicotinamide, DMF – dimethylformamide were synthesized according to the method [9]. The composition and structure of complexes were established basing on elemental analysis, IR spectroscopy and X-rays difraction [9]. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario El III elemental analyzer. The IR spectra were obtained in Vaselin on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range of 400-4000 cm^{-1}. The crystalline structure of complexes was determined on the Xcalibur CCD "Oxford Diffraction" diffractometer.

The quantum chemical study is widely used to explain the formation of molecular orbitals (OM) in the complexes of transition metals with different ligands

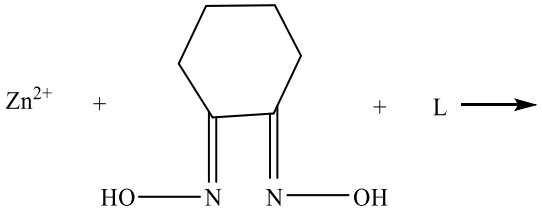
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and to analyze the chemical bonds within these compounds. It is known that coordinating the ligand to the metal ion leads to the displacement of electronic density and the modification of reaction capacity. The determination of the difference between the boundary levels of OM reagents (especially the HOMO and LUMO orbitals) can be useful for discussing the most favorable ways to get chemical reactions, because usually the reaction takes place between two centers that have a greater difference between electronic densities on boundary orbitals. In such a way it can be obtained important information about the bond character within the complexes of transition metals and the properties of these complexes.

The optimization of electronical structure and geometry of ligand molecules in the given nuclear configurations was performed *ab initio* using the SCF method in the *ROHF* approximation, using the 6-31G basis [10] for atomic functions. No symmetry restriction has been applied during optimization of geometry. To optimize complexes **1**-**4**, the GAMESS program package was used [8].

RESULTS AND DISCUSSION

As a result of the interaction of zinc acetate with 1,2-cyclohexanedione dioxime and a nicotinamide ligand, there were synthesized the mononuclear coordination compounds **1-4**, in which the dioxime chelate ligand bidentately coordinates within the zinc ion, while other ligands bind monodentately.



[Zn(CH$_3$COO)$_2$(NioxH$_2$)(S-Nia)(H$_2$O)].DMF (**1**)
[Zn(CH$_3$COO)$_2$(NioxH$_2$)(DMF)(H$_2$O)] (**2**)
[Zn(CH$_3$COO)$_2$(NioxH$_2$)(Nia)(H$_2$O)] (**3**)
[Zn(CH$_3$COO)$_2$(NioxH$_2$)(INia)(H$_2$O)] (**4**)

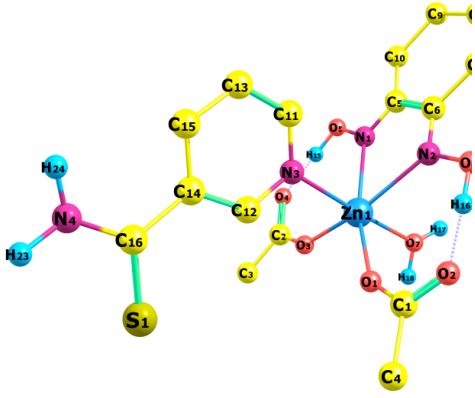
Fig. 1. Scheme of synthesis reactions of coordination compounds **1-4.**

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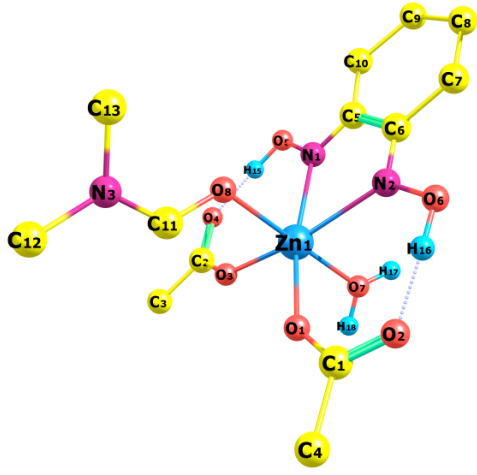
THEORETICAL RESULTS

Geometric structures

Optimization takes place in several stages, where for each coordinate modification the electron energy is calculated in the given nucleus configuration. There have been performed geometric optimization calculations for compounds **1-4** studied by *ab initio* HF with basic sets 6-31G, in singlet spin state and C_1 symmetry. The calculations reproduce the almost octahedral symmetry of the metal center observed at the decipherment of X-ray structures, the geometric parameters being close, with small deviations, to the crystallographic data. The geometric structures and parameters of complexes **1-4** are represented in Figure 2 and Table 1.

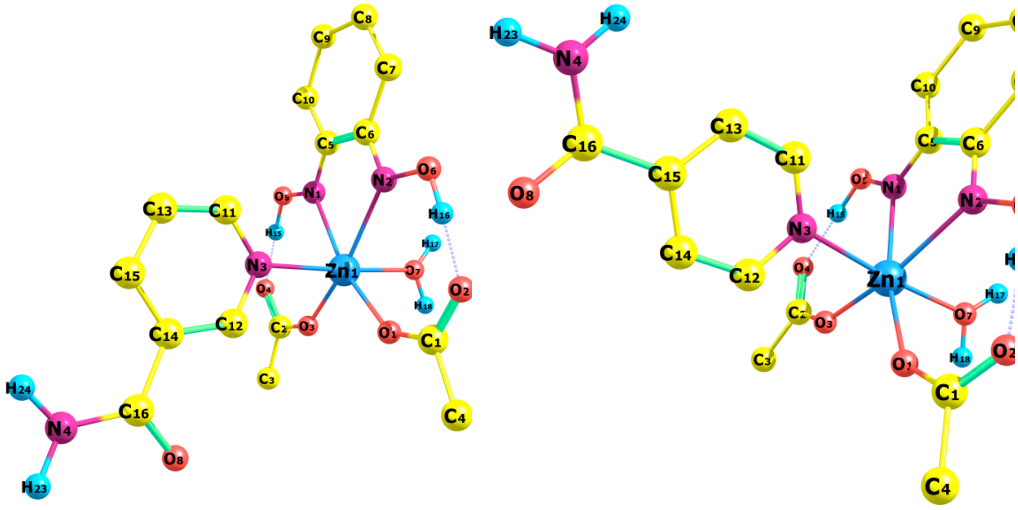


1



2

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3 **4**

Fig. 2. Geometric structure of complexes **1**-**4**.

The values of the distances between the central ion Zn1 and oxygen atoms O1, O3 (acetate), O7 (water), respectively nitrogen N1, N2 (oxime) and N3 (ligand), by which the bonds in compounds **1**-**4** are made, are shown in Table 1, that additionally presents the experimental values.

Table 1. Selected geometric parameters by X-ray and theoretical calculations at HF/6-31 of complexes **1**-**4** (theoretical/experimental [9]).

Compound	**R(Å), (theor./exp.)**			
	Zn-N_{ox}	**Zn-O_{ac}**	**Zn-O_{w}**	**Zn-L**
1	2.34/2.20	2.00/2.04	2.18/2.08	1.26/2.14
2	2.31/2.19	2.03/2.04	2.16/2.14	2.14/2.18
3	2.34/-	2.00/-	2.18/-	2.25/-
4	2.33/-	2.00/-	2.17/-	2.25/-

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The geometric parameters obtained on the basis of quantum-chemical calculations are close to the experimental ones, with small deviations. Theoretically, the distances between the central ions and the ligand Zn-N1, Zn-N2 in the oxime group and Zn-O1, Zn-O3 in the acetate are equal, which can not be experimentally proved, where the lengths of the bonds slightly differ (not essentially) due to complex packaging in the crystal. For complexes **3** and **4** experimental values are missing.

HOMO–LUMO energy gap and related molecular properties

The *ab initio* method is an important tool used to calculate the electron distribution in HOMO, LUMO boundary orbitals presented, respectively, in Figure 3 and 4. The energy values of OM and the gap-energy for compounds **1-4** are presented in Table 2.

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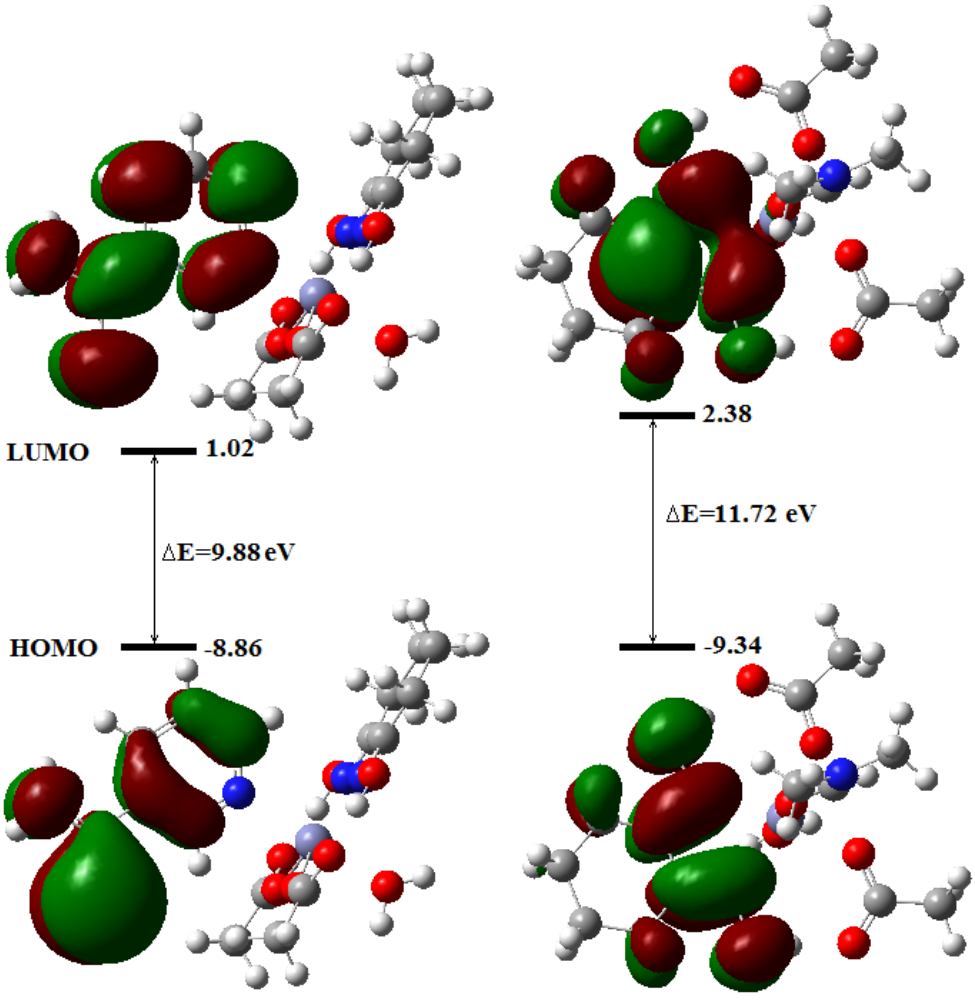


Fig. 3. Schematic representations of HOMO and LUMO molecular orbitals of the studied complexes **1** and **2** at the 6-31G.

The study of molecular areas for the two types of molecular orbitals (HOMO and LUMO), Figures 3 and 4, show the contribution of atomic orbitals to their formation. The value of E_{HOMO} energy is associated with the capacity to donate electrons to a molecule. Instead, the E_{LUMO} energy value is related to the electron

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affinity, respectively. The binding capacity of the ligand to the central ion (metal) increases with the increase of HOMO energy values.

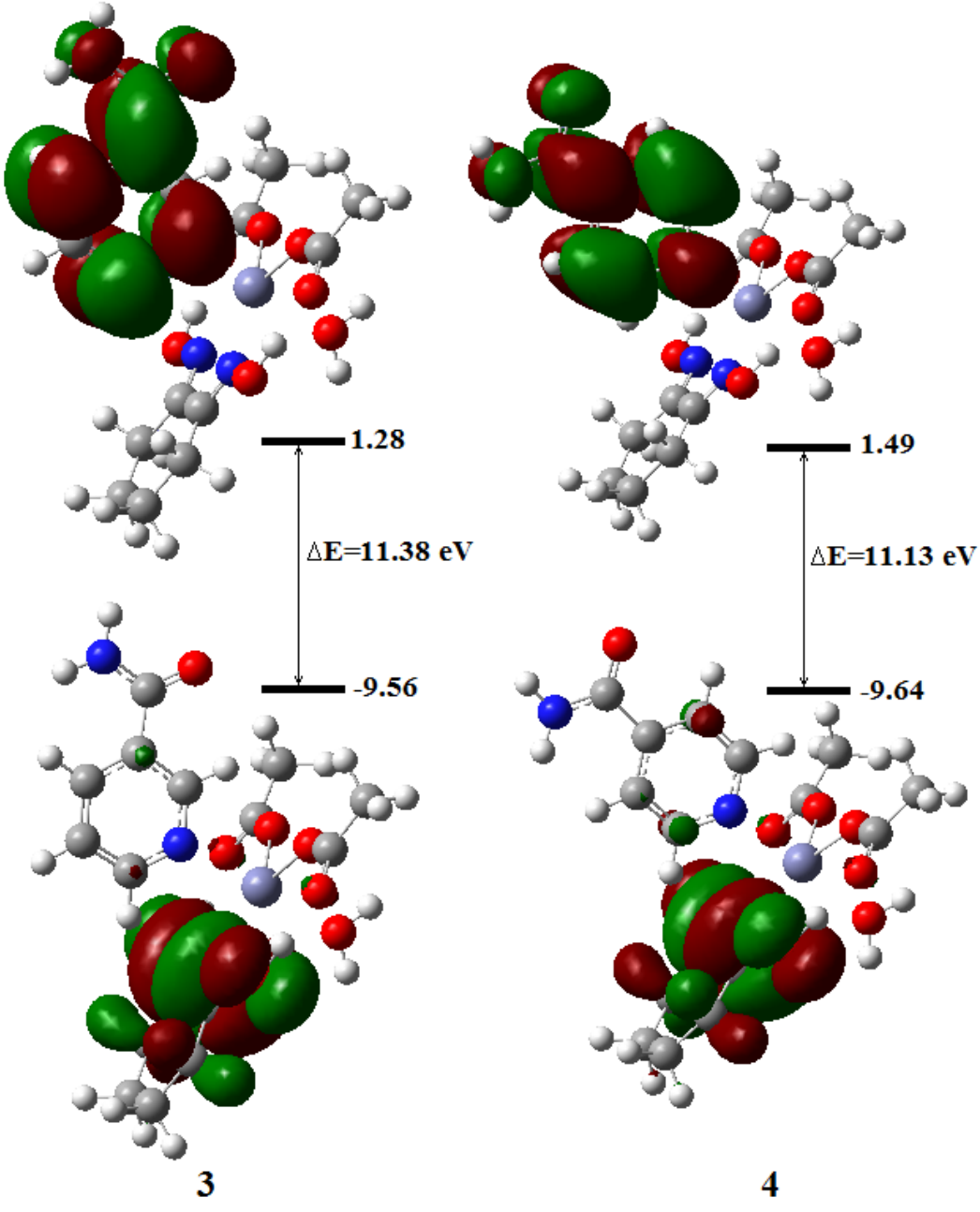


Fig. 4. Schematic representations of HOMO and LUMO molecular orbitals of the studied complexes **3** and **4** at the 6-31G.

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The energy difference between HOMO and LUMO levels ($\Delta E = E_{LUMO}$-E_{HOMO}) is also a chemically important molecular descriptor that explains the stability of the complex, one of its low values indicating that the molecule is highly reactive. Moreover, ΔE can be considered a critical parameter for assessing electrical properties of molecular transport. Concerning the energy difference between HOMO and LUMO orbitals, it can be observed that the most stable is complex **2**, having ΔE = 11.72 eV (Table 2).

Table 2. Calculated HOMO and LUMO energies and HOMO-LUMO gap energies in eV calculated at *ab initio* level using the 6-31G basis set.

Energy Parameters	**1**	**2**	**3**	**4**
$\mathbf{E_{HOMO}}$	-8.86	-9.34	-9.56	-9.64
$\mathbf{E_{LUMO}}$	1.02	2.38	1.82	1.49
$\mathbf{\Delta}E=\mathbf{E_{LUMO}}-\mathbf{E_{HOMO}}$	9.88	**11.72**	11.38	11.13
Total energy (a.u.)	-3536.18	-3046.11	-3213.53	-3213.53

The results obtained are consistent with similar complex compounds [11].

The HOMO and LUMO border molecular orbitals are important features that indicate how a molecule interacts with other chemical species. The HOMO molecular orbital acts as an electron donor while the LUMO orbital acts as an electron acceptor. Some general quantum descriptors that have been calculated by different quantum-chemical methods are: absolute electronegativity (χ), absolute rigidity (η) and softness (σ) Table 3 [12]:

$$\chi = -\frac{E_{LUMO} + E_{HOMO}}{2}, \qquad \eta = \frac{I - A}{2} \; and \; \sigma = \frac{1}{\eta}$$

where: I – ionization potential;

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A – electronic afinity.

According to Koopman's theorem [13] I and A are the energies of boundary orbitals, as follows:

$$I = -E_{HOMO} \text{ and } A = -E_{LUMO}$$

results:

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{\Delta E}{2}.$$

The measure of the ability to retain own electrons and capture foreign electrons is described by χ electronegativity. Hardness is a size that shows the opposition of an atomic or molecular system to the variation in electronic density in the system.

Another molecular parameter resulting from quantum-chemical calculations is the electrical dipole moment (μ), that is a measure of positive and negative electric charges separation in an electrical charge system, and thus a measure of system polarization. The dipole moment (μ) may also be related to the dipole-dipole interaction of molecules and the metal surface:

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2}$$

Using the dipole moment (μ) and absolute hardness (η) it can be calculated the general index of electrophilicity(ω) introduced by Parr [14]:

$$\omega = \frac{\mu^2}{2\eta}.$$

This parameter (ω) measures the sensibility of chemical species to accepting electrons. Thus the low values of (ω) suggest a good nucleophile, while the high values indicate the presence of a good electrophile. Table 3 exposes absolute electronegativity (χ), absolute rigidity (η), softness (σ), dipole moment (μ) and electrophilicity (ω) for the studied molecules.

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Table 3. Absolute electronegativity (χ), absolute rigidity (η), softness (σ), dipole moment (μ) and electrophilicity (ω).

Quantum Chemical Parameters	1	2	3	4
Absolute electronegativity χ (eV)	3.92	3.48	3.87	4.08
Ionization potential I (eV)	8.86	9.34	9.56	9.64
Electron affinity A (eV)	-1.02	-2.38	-1.82	-1.49
Absolute rigidity η (eV)	4.94	5.86	5.69	5.57
Softness σ $(eV)^{-1}$	0.20	0.17	0.17	0.18
Dipole moment μ (debye)	-3.92	-3.48	-3.87	-4.08
Electrophilicity ω (eV)	1.55	1.03	1.32	1.49

Mulliken atomic charges

One of the molecular properties immediately resulting from electronic structure calculations is charge distribution. Although there is no single definition of the number of electrons of an atom in a molecule, it has been found useful to carry out such a population analysis. Due to its simplicity, Mulliken population analysis (MPA) has become the most familiar method for counting electrons that are associated with a particular atom in a molecule.

The distribution of charge on atoms suggests the formation of donor and acceptor pairs involving the transfer of charge into molecule. Atomic charge is used to describe electronegativity equalization processes and charge transfer within chemical reactions. Mulliken charges of the atoms were calculated for each compound and are presented in Table 4.

Comparing the Mulliken charges on the ligand atoms connecting the central ion obtained from the optimized structure, it can be seen a higher negative value

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localized on the oxygen and nitrogen atoms connecting the central ion (Table 4). Hence, these atoms act as electron donors and in all cases there is an electrostatic attraction between the metal surface and the ligand molecules.

Table 4. Mulliken atomic charges calculated by HF/6-31G method.

1	**2**	**3**	**4**
q_{Zn}=1.47	q_{Zn}=1.42	q_{Zn}=1.47	q_{Zn}=1.47
q_{N1}=-0.34	q_{N1}=-0.35	q_{N1}=-0.34	q_{N1}=-0.33
q_{N2}=-0.34	q_{N2}=-0.35	q_{N2}=-0.34	q_{N2}=-0.33
q_{N3}=-0.79	q_{O1}=-0.86	q_{N3}=-0.79	q_{N3}=-0.76
q_{O1}=-0.86	q_{O3}=-0.86	q_{O1}=-0.86	q_{O1}=-0.86
q_{O3}=-0.86	q_{O7}=-0.86	q_{O3}=-0.86	q_{O3}=-0.86
q_{O7}=-0.86	q_{O8}=-0.74	q_{O7}=-0.85	q_{O7}=-0.85

Thus, using quantum-chemical calculations, four complex compounds were optimized. The main descriptors, such as ionization energy (I), electron affinity (A), HOMO-LUMO (ΔE) difference, dipole moment (μ), hardness (η) and softness (σ) were obtained from the *ab initio* calculations and used to identify differences in the stability and reactivity of the studied compounds.

Even if the calculations are performed in the gas phase and the experimental data are for the solid state, where the effect of the crystal field can affect the relative energies and geometric structures, the obtained quantum-chemical modeling calculations are consistent with the experimental ones.

Biological properties. As a result of microbiological tests, it was found that among complexes with 1,2-cyclohexanedione dioxime, after influence on this micromycete, **1, 3, 4** have a similar effect. The optimal concentration can be considered as 5 mg / L which allows growth by 42.79-57.14% (5th cultivation day) [9].

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CONCLUSIONS

The use of a complex set of research methods (chemical, physical, biological, computational) allows the complex and multilateral study of chemical compounds, which increases the probability of pupils/ students motivation for the analysis of complicated phenomena of nature. The studied model proposes the integration of experimental and theoretical methods using contemporary information technologies. We have described the synthesis of zinc complexes **1**-**4**. Structural data for these complexes revealed that a single coordination geometry is favored, by at least several u.a.e. Theoretical data, which were in good agreement with experimental data, indicated that the preference for creating a single coordination geometry was due to both steric and electronic effects. Quantum chemical calculations were carried out and there is a good correlation between the quantum chemical calculations and the experimentally obtained results.

The complex study model of chemical compounds is proposed for the university level, and for the pre-university level - in case the gifted pupils show interest.

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