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Sergiu Codreanu, Ion Arsene, Eduard Coropceanu

Active interdisciplinary research training context for developing innovative competence in chemistry

Introduction

Research training implementation requires the development of effective mechanisms that would allow the evolution from knowledge to experiment and from research to innovation. It depends on the teaching staff mastery at what stage and how to develop the research competence in school/university subjects. To develop successfully the research competence at the university level it would be desirable to train pupils with investigative activities at the school one. In the Republic of Moldova the subject of Chemistry at pre-university level is taught in the 7th-12th grades with a total volume of 442 academic hours of direct contact for the real profile. Only 36 hours (8.14%) of these are reproductive experimental activities which aim to consolidate the theoretical knowledge. Experimental activities of creative and scientific nature are not stipulated in the Curriculum. This situation leads to the excessive matter theorization in Chemistry and the lack of necessary evidence of the practical usefulness of the taught knowledge can create the impression of an unnecessary subject which diminishes the training level of young people to solve real situations in their daily life.

One of the ways to increase the attractiveness of Chemistry is to use the knowledge to solve specific situations of daily life. This field is characterized by an interdisciplinary approach because the phenomena in nature are subordinated to the laws of Physics, Chemistry, Biology, etc. A field in dynamic development is the use of IT in the training process [1-3]. The realization of the studies at the interdisciplinary boundaries highlights the most interesting phenomena and matter properties possible to be used in the elaboration of new technologies with higher characteristics than the existing ones.

Interdisciplinary studies are also valuable by involving research and interpretation methods from various fields, by using new technologies in new conditions and adapting them to specific requirements. As the energy status of molecular systems is of great importance for the proper development of chemical reactions, the use of quantum calculations proves to be a good exercise for determining the process likelihood and an efficient method for developing interdisciplinary research competence.

One of the interdisciplinary domains of Chemistry is Coordinating Chemistry, which allows the complexation of the inorganic and organic components generating new molecules with properties different from the initial substances. From the point of view of the practical applicability of the transition metal oximates, several directions are clearly emerging where the representatives of this class can be successfully used: the elaboration of artificial models of some vital biological molecules; development of biotechnologies for the targeted synthesis of microbial enzymes with wide use in various branches of the food, pharmaceutical and medicine industries; synthesis of materials with valuable physical properties (semiconductors, photo luminescent, dielectric, anticorrosive materials); obtaining systems used in hydrogen production, etc. [4-8]. One of the important tasks of the contemporary didactic methodology is to identify the links between education and research to create premises for implementing the research results in teaching and involving young people in the research process. A good solution would be to implement in the training process the methods that can be applied in both areas. The use of quantum calculations to determine the energy of some chemical systems and the process likelihood is a valuable element in motivating young people for training and research in Chemistry. The didactic method of studying molecules and phenomena within the school/university course as well as the use of more complicated study methods can be based on the use of several programs, one of them being GAMESS that contains different computation methods starting with those of molecular dynamics and mechanics, semicircular methods, *ab initio* methods based on Hartree-Fock theory, or methods based on functional density theory, and can be used to compute a very wide range of molecular properties [9].

The acquisition of quantum-chemical methods creates prerequisites for autonomous training, formation of a personalized style of thinking, and elaboration of some special solutions in a problem situation. Using the computer-based quantum-chemical methods we obtain an efficient and attractive interdisciplinary model: molecule/phenomenon - information technology support - quantum-chemical studies - motivation for training and development of specific skills in Chemistry and Computer Science.

Methods and materials

The new coordination compounds (complexes) were synthesized as a result of the interaction of inorganic salts with organic ligands in solutions with temperature and agitation according to the method [10]. The composition and structure of the coordination compounds were determined on the bases of elemental analysis, IR spectroscopy and X-ray diffraction [10]. 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 the coordination compounds was determined on the diffractometer Xcalibur CCD “Oxford Diffraction”.

For quantum-chemical calculations it was used the GAMESS computational program [9] containing a modern software package to state the electronic structure of the molecules to be studied. This program is used to investigate the structural properties and those determined by the electronic structure of molecules or complex molecular systems.

The electron structure and geometry of the ligand molecules in the respective nuclear configurations were modelled and optimized *ab initio* using the SCF method in the ROHF approximation using the 6-31G basis for atomic functions [11]. The quantum chemical parameters such as *EHOMO* (energy of the highest occupied molecular orbital), E_{LUMO} (energy of lowest unoccupied molecular orbital), ΔE (energy gap) and Mulliken charges were calculated and discussed.

As models, there were used molecules of zinc coordinate compounds based on 2-pyridinaldoxime and other auxiliary ligands. Both the energy status of some chemical systems and the energy profile of some intermediate reactions have been studied. There have been analyzed the coordination compounds $[Zn(CH_3COO)_2(paoH)_2]$ (**1**), $[Zn(paoH)_2(DMSO)_2][BF_4]_2$ (**2**), $[Zn(NCS)_2(paoH)_2]$ (**3**), where paoH is 2-pyridinaldoxime and DMSO is dimethylsulfoxide.

Results and discussions

In order to elaborate an efficient model of innovation competence development, it was analyzed the study mechanism of coordinating, i. e. composition, structure, energy status and biological properties to follow the path from simple chemical substances to complex molecules with various useful properties. An important objective was to use quantum-chemical calculations to study the energy state of the system, to develop the pupils and students' ability to use tools based on experimental and theoretical physico-chemical methods to modify the molecular design of the final substances and to forecast their properties and practical scope. These qualities would allow the development of the *Chemical Engineering* field with specialization in *the development of new materials with predicted properties*.

Coordination compounds differ in the wide spectrum of shown properties and zinc as a bio-element can confer biological properties to these complex molecules. In addition, the inclusion of organic molecules can enhance the action of these coordinating compounds on the physiological processes in different organisms. Both zinc, as a metal generating coordination compounds, and the used ligands offer broad diversification possibilities for the molecular composition and design of new compounds allowing the evolution from mononuclear complexes to coordination polymers with different physical, chemical and biological properties [12–15]. Thus, this paper-work purpose has an interdisciplinary character: the synthesis of new coordinative compounds with bio-stimulating properties, the investigation of their influence on some organisms, the study of the energetic state of the molecules and the identification of implementation methods of the results in the training process to develop the competence of research, innovation and practical application of scientific results.

As a result of the interaction of zinc salts ($Zn(CH_3COO)_2$ in case **1** or $Zn(BF_4)_2{\cdot}xH_2O$ in case **2** and **3**) with 2-pyridinaldoxime, there were synthesized mononuclear coordination compounds **1-3** (Fig. 1), in which the zinc ion coordinates the oxime ligand chelating bidentately and the other ligands bind monodentaly.

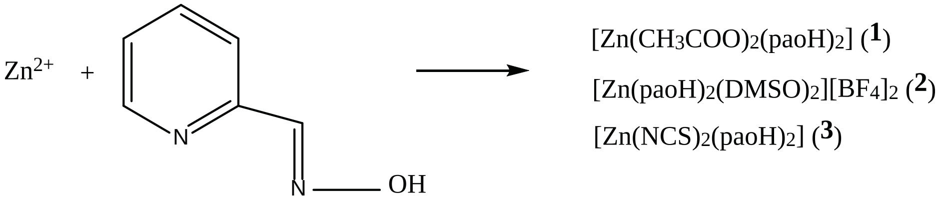


Fig. 1. Scheme of synthesis reactions of coordinative compounds 1-3.

Theoretical results

Geometric structures. The molecular and electronic structure for compounds **1–3** was investigated using *ab initio* calculations in S=0 spin state and C_1 symmetry. The calculations reproduce the almost octahedral symmetry of the metal centre also observed in the decipherment of X-ray structures while the geometric parameters are close to small deviations from the crystallographic data. The stable geometry and geometric parameters of coordinative compounds **1–3** are shown in Figure 2 and Table 1.

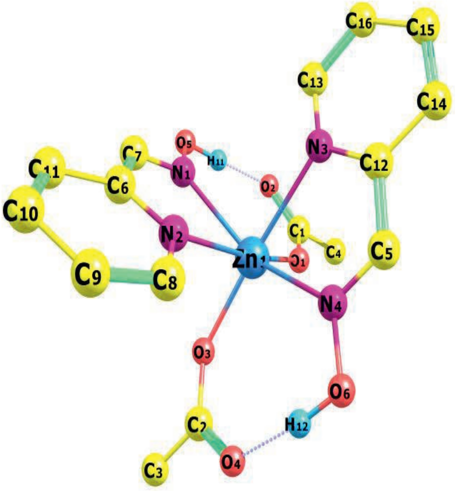
The distance values between the central ion and the O and N atoms through which the ligand is bound in compounds **1-3** are shown in Table 1, where the experimental values are also presented. At the same time, in the table below are shown the values of the total energies for these studied systems.

Table 1. Selected geometric parameters by X-ray and theoretical calculations at HF/6-31 of compounds **1–3** on the basis of paoH (theoretical/experimental [10]).

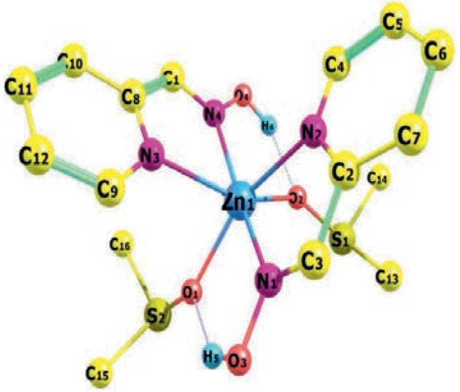
Compound	**R(Å), (theoretical/experimental)**			**Etot (a.u.)**
	Zn-Nox (Zn-N1, N4)	Zn-NPy (Zn-N2, N3)	Zn-L	
1	2.27/2.15; 2.16	2.37/2.21; 2.26	1.99/2.04; 2.03 (Zn-O1, O3)	-3060.38
2	2.16/2.12; 2.13	2.30/2.29; 2.17	2.15/2.09; 2.05 (Zn-O1, O2)	-3708.51
3	2.21/2.33	2.38/2.12	2.15/2.05 (Zn-N5, N6)	-3585.62

Analyzing the parameters obtained both experimentally and theoretically, we observe a fairly tight correlation with small deviations. Theoretically, the distances between the central ions and the Zn-N1, Zn-N4 oxime nitrogen atom, Zn-N2, Zn-N3 pyridine nitrogen atom and Zn-L are equal, but for experimental data the bond lengths are slightly (insignificantly) different due to packing the compound in crystal and as a result of different interactions.

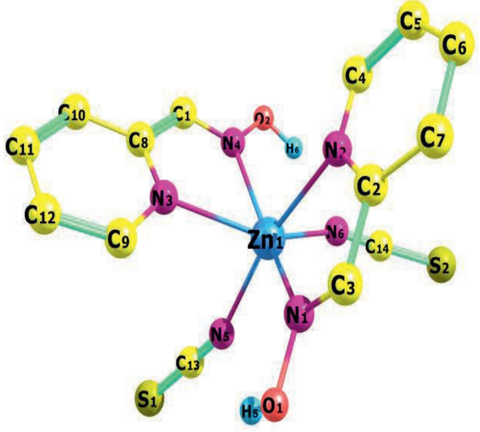
HOMO–LUMO energy gap and related molecular properties. For coordinative compounds **1-3** it was calculated the distribution of electrons on border orbitals HOMO and LUMO and they were presented respectively in Figure 3. The energy values of OM and gap-energy are shown in Table 2. For coordinative compound **1**, HOMO and LUMO are located on 2-pyridinal doxime ligand.



Compound **1**



Compound **2**



Compound **3**

Fig. 2. Molecular structures of coordination compounds 1–3

The study of molecular areas for the two types of molecular orbitals (HOMO and LUMO), Figure 3, shows the contribution of atomic orbitals to their formation. The E_{HOMO} energy value is associated with the ability to donate electrons to a molecule, and respectively with its oxidation tendencies.

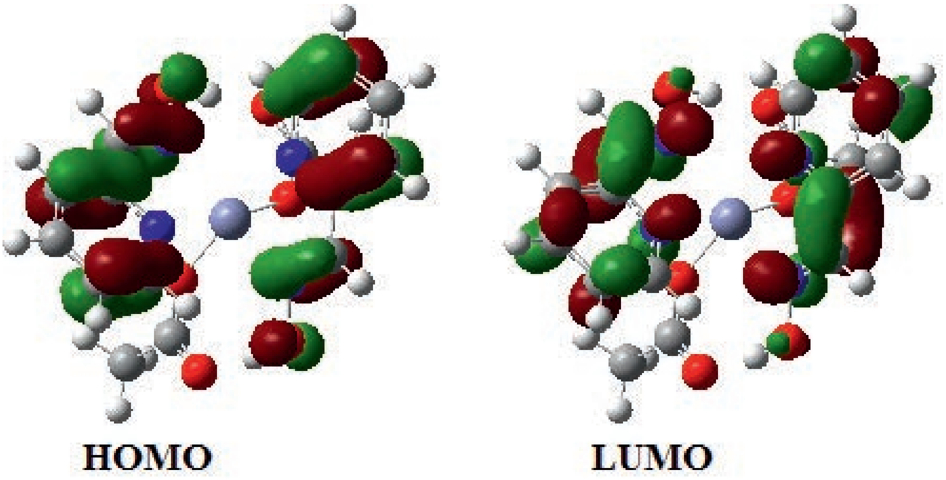


Fig. 3. Schematic representations of HOMO and LUMO molecular orbitals of the studied coordination compound 1 at the 6-31G.

Instead, E_{LUMO} energy value is related to the electron affinity and respectively to its reduction tendencies. The ability to bind the ligand to the central ion (the metal) increases while increasing HOMO energy values. The calculations show that the parameters obtained for compound **1**, the HOMO and LUMO levels are equal to -9.62 eV and 1.53 eV.

The energy difference between HOMO and LUMO levels ($\Delta E = E_{LUMO}-E_{HOMO}$) is also a chemically important molecular descriptor explaining the coordinative compound stability. A low value indicates that the molecule is extremely reactive. From the values presented in the table, the most stable is coordinative compound **1**, having ΔE = 11.15 eV (Table 2).

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

Compound	E_{HOMO}	E_{LUMO}	ΔE
1	-9.62	1.53	11.15
2	-15.11	-4.05	11.06
3	-8.04	0.71	8.75

The obtained results are consistent with similar coordination compounds [16].

The sum and difference of the boundary molecular orbital energies are correlated with the chemical reactivity of the molecules by generic quantum descriptors: absolute electro-negativity (χ), absolute rigidity (η) and softness (σ) Table 3 [17–19]:

$$\chi = -\frac{E_{LUMO} + E_{HOMO}}{2}$$

$$\eta = \frac{I - A}{2} \ and \ \sigma = \frac{1}{\eta}$$

where: I – ionization potential;

A – electronic affinity.

According to Koopman's theorem [20] I and A are the energies of border orbitals as follows:

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

results:

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

The electron yielding tendency is described by the electro-negativity. Hardness is a measure that describes the opposition of an atomic or molecular system to the electronic density variation in the system.

Another molecular parameter resulted from quantum-chemical calculations is the electrical dipole moment (μ), which reflects the partial separation of the electrical charge into molecules:

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

The dipole moment (μ) is another parameter of electronic distribution in a molecule that can be related to the dipole-dipole interaction of molecules and metal surface. This parameter is a measure of the molecular system polarization.

Using μ and η, it can be calculated the general electrophilicity index (ω) that was introduced by Parr [21]:

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

According to this parameter, electrophilicity index value (ω) measures the chemical species sensitivity of accepting electrons. So, the low values of (ω) suggest a good nucleophile, while higher values indicate the presence of a good electrophile.

Table 3 shows the absolute electronegativity (χ), the absolute rigidity (η), the softness (σ), the dipole moment (μ) and the electrophilicity (ω) for the studied molecules.

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

Compound	χ	I	A	H		μ	ω
1	4.05	9.62	-1.53	5.58	0.18	-4.05	1.47
2	9.58	15.11	4.05	5.53	0.18	-9.58	8.30
3	3.67	8.04	-0.71	4.38	0.23	-3.67	1.54

Mulliken atomic charges. The value calculation of Mulliken atomic charge has an important role to play in applying a quantum-chemical study for a molecular system such as the dipole moment effect, molecular polarization, electronic struture, and a multitude of properties of molecular systems. The distribution of the charge on atoms suggests the formation of donor and acceptor pairs involving the transfer of the charge into the molecule. Atomic charge is used to describe processes of electronegativity equalization and charge transfer in chemical reactions. Mulliken atomic charges were calculated for each compound and presented in Table 4.

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

1	2	3
q_{Zn}=1.47	q_{Zn}=1.53	q_{Zn}=1.46
q_{N1}=-0.31	q_{N1}=-0.39	q_{N1}=-0.32
q_{N2}=-0.74	q_{N2}=-0.79	q_{N2}=-0.74
q_{N3}=-0.74	q_{N3}=-0.79	q_{N3}=-0.74
q_{N4}=-0.31	q_{N4}=-0.39	q_{N4}=-0.32
q_{O1}=-0.84	q_{O1}=-0.98	q_{N5}=-0.78
q_{O3}=-0.84	q_{O2}=-0.98	q_{N6}=-0.78

By comparing Mulliken atomic charges on the ligand atoms connecting to the central ion and obtained from the optimized structure, the highest negative value is located on the oxygen and nitrogen atoms connecting to the central ion (Table 4). So, these atoms act as electron donors and in all cases there is an electrostatic attraction between the metal surface and the ligand molecules.

Thus, using the quantum-chemical calculations, three coordinative compounds were optimized. The main descriptors, such as ionization energy (I), electron affinity (A), difference HOMO-LUMO (ΔE), dipole moment (μ), hardness (η) and softness (σ) were derived out from DFT 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 modelling calculations have a good correlation with the experimental ones.

Biological properties. As a result of microbiological tests it was found out that compound **1** at concentrations of 5-10 mg/L may be used as a biosynthesis stimulator of ordinary amylase (pH 4.7) by the micromicete *Aspergillus niger* CNMN FD 06 [10]. The introduction of coordinating compound **1** into the cultivation medium stimulates the enzyme genesis processes by 35.63% on day 5 and 33.85% on day 6.

Conclusions

The mechanism of developing innovative competence in Chemistry, along with the acquisition of new compounds useful in various fields, requires the involvement of a complex system based on experimental and theoretical methods. There has been proposed a model for integrating the synthesis of the new compounds and their study by various methods, particularly by quantum-chemical calculations, which can reflect a number of aspects of the energetic state of the molecular systems and allow development prognosis of some processes, the stability of compounds in different environments, the possibility of performing some substitution processes, etc., as well as the determination of some areas of practical utility.

We have described the synthesis and the characterization of zinc compounds (**1-3**). Structural data for these compounds revealed that single coordination geometry is favoured, by at least several a.u. Theoretical data, which were in good agreement with the experimental ones, indicated that the preference for creating a single coordination geometry was due to both steric and electronic effects. Quantum chemical calculations have been carried out and there is a good correlation between the quantum chemical calculations and the experimentally obtained results.

The analyzed model can be proposed as a compulsory one to be studied in the Chemistry university programs, as well as optional for the gifted pupils in pre-university education. This mechanism allows a more efficient integration of the Education-Research fields and motivates for conscious and co-interested training developing specific Chemistry and Informatics competencies. On the basis of this methodology differentiated and individualized instruction can be promoted for effective exploitation of the intellectual potential of each pupil/student.

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Active interdisciplinary research training context for developing innovative competence in chemistry

Abstract

The development of motivation mechanisms for training is an important objective of contemporary didactics in the field of exact and nature sciences. Effective integration models of the fields of Education, Research and Practical Application are required in order to involve pupils and students in the study of Chemistry. It is proposed a model which describes the algorithm from chemical synthesis to the study of composition, structure, energy state and determination of practical application areas. These stages/operations develop specific skills in Chemistry and motivate for fundamental and conscious interdisciplinary training.

Key words: research training, quantum calculations, interdisciplinary study, zinc compounds.

Sergiu Codreanu, PhD student
Tiraspol State University, Republic of Moldova
email: codreanu_sergiu@mail.ru

Ion Arsene, PhD, associate professor
Tiraspol State University, Republic of Moldova
email: arsene.ion@ust.md

Eduard Coropceanu, PhD, professor
Tiraspol State University, Republic of Moldova
email: ecoropceanu@yahoo.com