Available online at www.sserr.ro
Social Sciences and Education Research Review

(7) 1 194 - 211 (2020) ISSN 2393–1264
ISSN–L 2392–9863

USING OF THE STUDY ON ENERGY PROFILE IN THE PREDICTING OF THE SUBSTITUTION REACTION OCCURRING AT THE CHEMISTRY COURSE

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Abstract

In order to achieve a modern, formative education, we consider the process of interdisciplinary teaching-learning-assessment of chemistry an important and determinant factor. Interdisciplinary study of content on different educational disciplines will substantially contribute to the education of chemistry students, to the formation and development of chemistry-specific skills, of a logical and flexible thinking, to a better fixation and systematization of theoretical knowledge and their ability to apply practice. To this effect, the use of different programs of molecular energy calculation, of some chemical processes arising in the analysed systems, of structure visualization, etc. requires an interdisciplinary approach to knowledge, skills and abilities in the field of chemistry in particular, as well as in computer science, physics, mathematics. This interdisciplinary approach presents a challenge and, at the same time, a necessity for chemistry students as future specialists in the educational field.

Keywords: interdisciplinarity, energy study, specific competence, radical reaction, ligand, coordinating compound, substitution.

Introduction

In modern education, more and more interconnected trends in the curricular content appear. This need for integration arises from the impossibility of one of the disciplines (e.g. biology, chemistry, physics, mathematics, geography, etc.) to solve or explain some complex problems of processes and phenomena related to the unitary content of life and the surrounding world.

The interrelation of the contents of Chemistry discipline with Biology, Physics, Mathematics, Geography, and Computer Science in the educational process is based on cultivating students' mastery of the skills necessary to effectively adapt future specialists in different social situations. The gained knowledge will have a greater value if it is practiced in real-life problem solving. In an interdisciplinary context there are opportunities for horizontal transfer of knowledge from one discipline to another at methodological and conceptual level.

Interdisciplinarity is a methodological principle of an integrated approach to chemistry through the formation at students of an integrated knowledge system based on methods and principles of investigation for the development of integrated, and unitary thinking [1].

The process of teaching-learning-assessment of chemistry at university level is a complex one and aims at building competencies in a certain field, independent of achievements got earlier in other areas of knowledge. Therefore, the interdisciplinary approach of content from different disciplines of study leads to the creation of a favorable and necessary environment for the

developing of the initial professional competence at chemist students in an inter-/transdisciplinary context [2].

The Chemistry training will be much more effective if the interdisciplinary reference is made. In the study of such discipline as *Chemistry*, for example, at the university stage of teaching-learning, some interdisciplinary connections with other related disciplines, such as: geochemistry, physical chemistry, coordinating chemistry, organic chemistry, analytical chemistry, etc., are established. [3].

The interdisciplinarity is an effective way of organizing curricula at all levels, which goes beyond the area of disciplinary content and which targets the area of methods/attitudes. The process of attaining an interdisciplinary model results from the intersection of different disciplinary areas, being ignored the strict limits of the disciplines. Through an interdisciplinary approach, higher learning objectives (metacognitive capacities) can be achieved. The organizer principle is no longer focused on content (as in the case of multidisciplinarity) but focuses on key competences [4].

One of the ways to increase the attractiveness of chemistry is to use the knowledge to solve real-life situations. This field is characterized by an interdisciplinary approach, because the phenomena occurring in nature are subordinated to the laws of physics, chemistry, biology, etc. The use of information technologies in the training process becomes a field under dynamic development [5, 6].

The reform of Moldovan education has created prerequisites for some transformations in the curriculum, where the interdisciplinary perspective is distinguished. The society needs specialists who must have the ability to think interdisciplinary and easily move from one domain to another. The study of interdisciplinary correlations has always been in the view of methodologists, while the integrated study of disciplines has raised the issue to a much higher level. The integration of disciplines is important in the training process of

highly qualified specialists. At a global level, the training of staff is focused towards the formation of highly qualified specialists who potentially can be employed in several adjacent areas.

At the school/university curriculum level, there are sufficient resources to achieve interdisciplinary education, where common objectives with more disciplines can be established. Interdisciplinary education aims to establish an integrated curriculum, i.e. an organization of the educational process in which pupil/student performs activities which require skills acquired not only in a school/university discipline. The correlation between disciplines can be achieved at the level of content, objectives, creating a favourable environment for each pupil / student to express freely, to work in a team or individually.

During the study of Chemistry, the student learns different chemical processes that occur between the interacting compounds, one of which is the *substitution process*. Substitution (replacement) is a chemical reaction by which an atom or a radical of a compound is replaced by another atom or radical derived from another chemical body [7].

The modern educational process is marked by the active implementation of advanced technologies that would allow the study in an attractive and interactive context of bodies, phenomena, etc. The realization of the studies at the interdisciplinary boundaries highlights the most interesting phenomena and properties of the matter, which can be used in the elaboration of the new technologies with more superior characteristics than the existing ones.

The interdisciplinary studies are also valuable by involving research and interpretation methods of various fields, by using new technologies in new circumstances, adapting them to actual requirements. Because in the field of chemical reactions the energy state of the molecular systems is of a great importance, the use of quantum calculations come to be a good exercise for determining the probability of carrying processes and an efficient method of developing interdisciplinary research competence.

It is necessary the teacher to have truthful arguments based on calculations and experimental data to persuade the disciples of the fairness of the processed information, but it is even more important for the pupils/students to have themselves the skills to carry out these operations. The use of quantum calculations to determine the energy of some chemical systems and the probability of carrying out of some processes is a valuable element in motivating young people for chemistry training and research.

Applied methods and materials

The geometric structure of the reactants (R), transition states (TS) and reaction products (P) were studied *ab initio* using the SCF method in the ROHF approximation, using for the atomic functions the base 6-31n (ROHF/6-31G(d)) [8].

Using some methods of theoretical calculation, a series of geometric and energy parameters related to the molecular structure and the energy profile of some chemical processes can be correlated and predicted. The use of quantum-chemical methods in the pre-university educational system would allow the creation of a set of valuable skills for some pupils who could later develop their own research style based on information technologies and rapidly evolving electronic resources. The studied model allows the harmonious intercalation of the training with the research [9], thus the trainee gets the opportunity to acquire professional skills useful for solving different problems in the field, as well as in the related fields.

All calculations were performed using GAMESS [10], which is a modern software package used to investigate structural properties or those determined by the electronic structure of molecules or complex molecular systems.

GAMESS is used not only for the study of the geometry of the molecules but also of the reactions with their participation, for the study of intermolecular

interactions and the energy profile, being especially useful for reactive molecular species that are difficult or even impossible to study through experimental methods. This study of energy in molecular systems is entirely based on quantum-chemical calculations as well as their theoretical processing, procedures which can be recommended to pre-university teachers for implementation in professional practice. The GAMESS program performs the calculations based on the input data. All the program parameters are introduced in the initial files (example of the transition state calculation shown below):

```
$contrl scftyp=rohf runtyp=sadpoint icharg=0 mult=2 $end
 $contrl maxit=200 $end
 $system memory=10000000 timlim=2200 $end
 $statpt nstep=200 hess=calc $end
 $basis gbasis=n31 ngauss=6 $end
 $guess guess=huckel $end
 $scf damp=.true. $end
 $data
 [CH3-H-Cl]
 Cnv 3
 C       6.0   0.0000000000   0.0000000000   0.0671388126
 H       1.0   0.0000000000   0.0000000000   1.9032760811
 H       1.0   1.0676901532   0.0000000000  -0.0247742350
 Cl     17.0   0.0000000000   0.0000000000   3.8039078114
 $END
```

Using this model, the calculations were performed for all species involved in this radical substitution reaction.

The didactic method of studying molecules and phenomena within the school / university course as well as for applying more complex study methods can be based on the use of several programs, one of them being GAMESS,

which contains different calculation methods, starting with those of dynamics and molecular mechanics, semi-empiric methods, methods *ab initio* based on Hartree-Fock theory or methods based on the theory of density function and can be used for calculating a very wide range of molecular properties [10].

As the example, the reactions of methane chlorination occurring in the radical substitution process, resulting from the mechanism of the radical chain reaction and substitution reactions of some ligands from coordinating compounds have been taken. Both the energy status of the investigated chemical systems and the energy profile of the intermediate reactions were studied. The acquisition of quantum-chemical methods creates prerequisites for autonomous training, the formation of a personalized style of thinking, the elaboration of some special solutions in a problem situation.

Results and discussions

Theoretical study of the substitution reaction of hydrogen by halogen

The subject of this study is proposed radical reactions to some hydrocarbons. Most often, the free radical represents a carbon atom with an orbital partially occupied by an electron (a unpaired electron). Such a species is the result of a homolytic cleavage and has the character and behaviour of a monovalent atom. Free radicals being particles with relatively high reaction capacity have a fairly short life span. In their stabilization tendency they are combined in twos or through reactions with other substances present in the system. Such radicals are initiators of radical-mechanism reactions (addition, substitution or polymerization). We can refer to radical substitution reactions (SR), in which a free radical extracts an atom from a stable molecule, transforming the latter into a new free radical (examples):

$Cl^{\bullet} + H_2 \rightarrow HCl + H^{\bullet}$

$CH_3^{\bullet} + CCl_4 \rightarrow CH_3Cl + CCl_3^{\bullet}$

$CH_3^{\bullet} + H_3C–R \rightarrow CH_4 + H_2C^{\bullet}–R$

Reactions of this type result from the mechanism of the transition state with low activation energy (0-5 kcal/mol), in the end the reaction rate being quite high:

$$\underset{\text{Substrate}}{AB} + \underset{\text{Reagent}}{C} = \underset{\text{Transition state}}{[A \cdots B \cdots C]} = \underset{\text{Reaction product}}{A + BC}$$

In the free radical reactions besides the stable reaction product, a new free radical is formed. This, in turn, can initiate a new substitution reaction, in which besides a stable new molecule a new free radical is formed. Consequently, the state of the radical can continue through a large number of reactions, thus creating a chain reaction.

Chain reactions have specific properties that distinguish them from other types of reactions and thus become recognizable. A chain reaction consists of the following steps: initiation, propagation, termination (interruption).

Halogenation of alkanes, according to the nature of the process being carried out, is a radical substitution reaction (SR), which proceeds fairly easily in the case of the inferior representatives of the homologous series and slower in the case of the superior ones. The reaction is initiated at light (hν) or temperature (300-600°C). In these reactions the hydrogen in the alkane molecule can be replaced by halogen (especially chlorine or bromine, fluorine reacts quite energetically; iodine - not) to a complete substitution. The halogenation reaction of methane is a chain one and takes place in several stages: under the action of light or temperature, the chlorine molecule is homologously cleaved with the formation of two chlorine radicals. The resulted chlorine radicals react with the methane molecule forming hydrogen chloride and free radicals of methyl. In turn, methyl free radicals react with

other chlorine molecules, forming methyl chloride and free chlorine, which reacts again with methyl chloride. Thus, the initiated reaction can proceed to the end (complete substitution).

Thence we have:

1. initiation of the reaction:

   $Cl \bullet \mid \bullet Cl \rightarrow Cl^{\bullet} + Cl^{\bullet}$

2. propagation of the reaction:

   $CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$

   $CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

   $CH_3Cl + Cl^{\bullet} \rightarrow CH_2^{\bullet}Cl + HCl$ etc.

3. interruption of the reaction:

   $CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3–CH_3$

   $Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

   $CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$.

Also, with the help of quantum-chemical calculations, one can study the energy profile of some intermediate reactions that take place in different processes, for example substitution in the chlorination reaction of methane.

Particular case is the radical substitution reaction $CH_4 + Cl_2 = CH_3Cl + HCl$ for which the intermediate reactions were studied and theoretically analyzed; according to the reaction equation. the energy profile was studied. The process consists of the following steps:

1. At the first stage, which is the initiation reaction carried out under the action of light or temperature; the homolytic cleavage of the chlorine molecule takes place with the formation of two free radicals:

$$Cl_2 \overset{h\nu}{\rightarrow} 2\dot{C}l$$

From the energy point of view, this reaction is thermodynamically convenient (exothermic), ΔE = 7.81 kcal / mol.

2. Several intermediate reactions may occur at the propagation stage of the radical chain:

   a. The interaction of methane with the chlorine radical with the cleavage of the covalent bond C-H, with the initial obtaining of an intermediate (ST) with the following structure $CH_3 \cdots H \cdots Cl$, with the imaginary frequency 1731,6i, finally obtaining the reaction products and forming a new radical according to the reaction equation:

$$CH_4 + \dot{C}l \rightarrow CH_3 \cdots H \cdots Cl \rightarrow \dot{C}H_3 + HCl$$

Figure 1 schematically shows the energetic profile of this radical reaction:

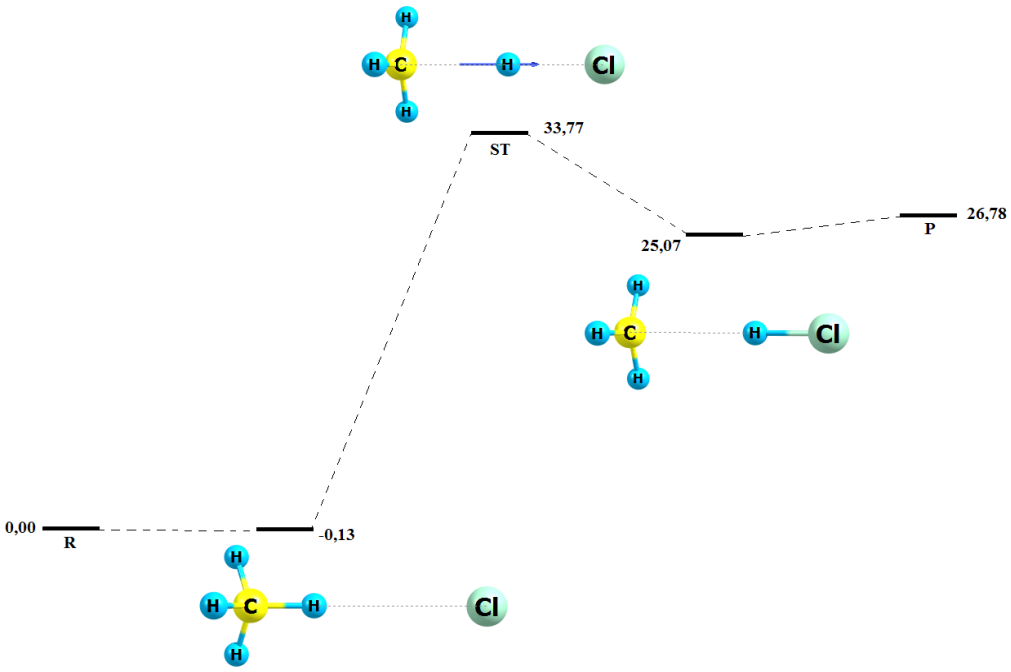

Fig. 1. Energy profile of $CH_3^{\bullet}$ radical formation through the interaction of methane with $Cl^{\bullet}$ radical.

According to the calculations, it turned put that the pre-reaction complex has a binding energy of -0.13 kcal/mol, the transition state energy is 33.77 kcal/mol, and the post-reaction complex has a stabilizing energy of 25.07 kcal/mol. The energy which triggered this reaction has a value of 33.64 kcal/mol. The vector of transition state, associated with the unique imaging frequency, is first of all a movement of the hydrogen atom H between C and Cl that represents state structure appropriate to transition.

b. The methyl radical formed at the previous step interacts with another chlorine molecule to form an intermediate $CH_3 \cdots Cl \cdots Cl$, which possesses only one imaginary frequency with a magnitude of 534.8 cm^{-1}. The obtained reaction products are the chloride radical and methyl chlorine according to the equation of reaction:

$$\dot{CH_3} + Cl_2 \rightarrow CH_3 \cdots Cl \cdots Cl \rightarrow CH_3Cl + \dot{Cl}$$

Figure 2 shows the location of the transition state from reactants to products and also shows the energy profile of the reaction. In order to get an insight into reaction mechanisms and to support experimental activity, theoretical studies of energy calculations and identification of transition state structures and pre- and post-reaction complexes were undertaken. This structure (ST) is characterized by the partial transfer of the chlorine atom to the methyl radical:

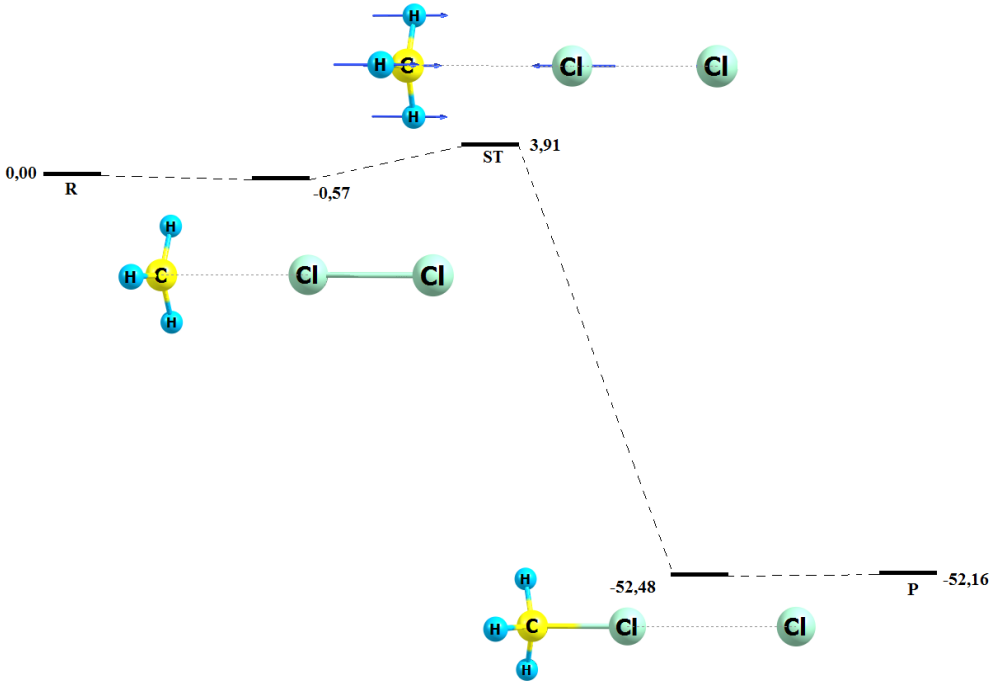

Fig. 2. Combination reaction of the methyl radical with the chlorine molecule.

The calculations show that the pre-reaction complex has a binding energy of -0.57 kcal/mol, the transition state has energy of 3.91 kcal/mol and the post-reaction complex has a stabilizing energy of -52.48 kcal/mol. The obtained result indicates a less stable complex of transition state than reactants and a barrier of activation of this reaction with a value of 3.34 kcal/mol.

3. Interaction between the radicals obtained at the previous stages may also be considered as a stage of interruption of the studied reactions with obtaining the ethane molecule, chlorine or methyl chloride. By analysing these reactions, it was theoretically proved that the combination of radicals actually takes place with the formation of neutral molecules and they occur without any reaction barrier.

The method is proposed for the Organic Chemistry course (cycle I) while studying the energy of radical substitution processes and is optionally recommended for the high school cycle.

Theoretical study of the substitution reaction of some ligands in coordinating compounds

Inorganic chemistry studies different substitution reactions, which differ in the interacting compounds, the used substituents, the mechanisms of chemical reaction, and so on.

By studying the substitution reactions, can be determined the result or the products to be obtained, the mechanism of the reaction (splitting of one type of chemical bond with the formation of another type), the different reactivity of the investigated compounds with different reactants, the state of aggregation of the system in which can occur reaction. In order to make the teaching-educational process more effective at chemistry course can be used different *methods* of scientific knowledge (problem-solving, modelling, schematization, chemical experiment, analysis, synthesis, generalization, etc.) and various *didactic resources*, including computer and the digital software necessary for selecting, viewing, processing and presenting new information.

The use of different digital software in the study of Chemistry is necessary to deepen the theoretical knowledge in the field, to form and develop practical skills for their further application, and to deepen the understanding of the processes and phenomena that arise in the analysed systems. The organization of an interdisciplinary education better targets both scientific progress and socio-human requirements regarding the formation of a contemporary personality, helps to gain an overview of life and universe, to thoroughly assimilate fundamental values and easier to distinguish objectives.

In order to analyse the possibility of an interdisciplinary investigation, involving knowledge from the fields of chemistry, physics, informatics, , it

was proposed the study of the energy process of the substitution of some sulphanilamide ligands (SAM) from coordinating compounds with other ligands (L – in current study – bipyridyl).

Quantum-chemical calculations were performed to determine the electronic structure of the coordinating compounds and the ligands in their composition. The geometric parameters calculated in the fundamental state of the studied compounds and the experimental data are presented in Table 1. The comparative analysis (Table 1) proves a good correlation of the theoretical and experimental data regarding the lengths of the chemical bonds formed between the cobalt atom and the atoms of the elements that coordinate to it on the apical axis.

Table 1. Theoretical and experimental geometric parameters (Axial co-ligand).

Complex	Theoretical values, Å		Practical values, Å	
	R (Co-E_L)	*R* (Co-N_{azid})	*R* (Co-E_L)	*R* (Co-N_{azid})
1	2,03	1,94	1,961(4)	2,031(4)
2	2,03	1,94	1,969(6)	2,024(6)

Since for the synthesis of coordinating compounds **1** and **2**, as rectangles, are used complexes from which the sulphanilamide ligands are substituted [9], it was decided to calculate the energy profile for these reactions. Studying these two substitution reactions quantum-chemically, where we have the same reactants, but in different reaction conditions different products (Figure 3) are obtained, the energy parameters described in Table 2 were described.

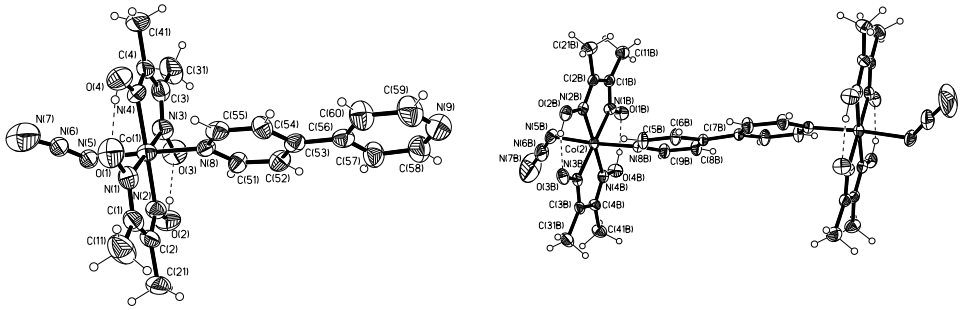

Fig. 3. The molecular structure of the complexes **1** (a) și **2** (b) [11].

The energy difference ($\Delta E = \Sigma E_P - \Sigma E_R$) between the reactants and the reaction products for each substitution is calculated. The obtained results indicate the exothermic nature of the substitution reactions.

Table 2. Energy profile of substitution reactions

Nr.	The substitution reaction	ΔE (kcal/mol)
1	$[Co(N_3)(DH)_2L_1] + bpy \rightarrow [Co(N_3)(DH)_2bpy] + L_1$	-9.22
2	$2[Co(N_3)(DH)_2L_1] + bpy \rightarrow [(Co(N_3)(DH)_2)_2bpy] + 2L_1$	-14.18

For both reactions the energy profile was studied. In the case of the first reaction, the reaction energy is -9.22 kcal/mol, and for reaction nr. 2 the reaction yield is 14.18 kcal/mol. Figure 4 shows the substitution reaction scheme:

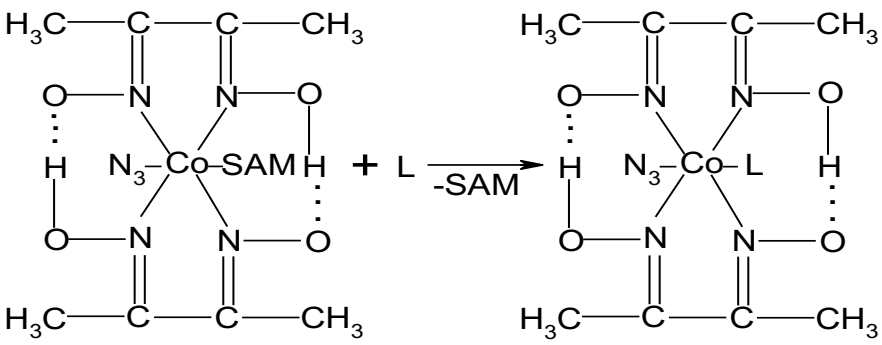

Fig. 4. Scheme of substitution reaction of the ligand SAM from the internal sphere of the complex by L.

Also, on the basis of the substitution reactions, it was decided to be calculated the energy of the cobalt bond with the sulphanilamide ligand prior to substitution as well as the substituent ligand in the final compounds. Table 3 shows the binding energy in the optimized geometric configuration, which is determined according to the relationship:

Table 3. Connection energy $R_{Co\text{-}L}$.

Ligand	$E_{bond.}$(e.a.u.)	$E_{bond.}$(kcal/mol)
SAM (L_1)	0.0678	42.54
bpy	0.0871	54.66

The method is proposed for the study of the substitution process energy and it is recommended for undergraduate and master degree courses, especially for Basics of Coordination Chemistry (Cycle I) and Coordination and supramolecular Chemistry (Cycle II).

Conclusions:

A quality education aims to develop students' systemic, integrative thinking about life and, as a result, it appears the need for the formation and development of integrated competencies which allow the correlation of the specific content of several disciplines, the transfer of knowledge and methods from one discipline to another.

The degree of student preparing for life is directly proportional to their ability to contextualize and apply knowledge in actual life situations, to solve everyday problems engaging different disciplines. The use of calculation methods of the energy of ligand substitution processes in coordinating compounds provides the opportunity to study the competition processes of different molecules at coordination with the central ion, the fact which allows subsequent analysis of the causes and the formulation of the conclusions regarding the degree of probability of formation of some coordinating compounds on the ground of theoretical calculations.

The training of the skills to use interdisciplinary methodology that integrates elements of chemistry, physics and informatics creates prerequisites for complex and profound studies in order to elucidate the chemical processes based on the calculation of the energy state of the molecular systems. This process enables students to build competences in the field of study subjects and information technologies.

The quantum-chemical calculations allow determining the energy profile of some chemical reactions, the fact which allows us to have a real prognosis in terms of the possibility of carrying out the chemical process.

Thus, using computer-based quantum-chemical methods, we achieve an efficient and attractive interdisciplinary model that argues the necessity and usefulness of conscious chemistry training. The model is recommended for use in university courses, and optionally in general education, for teaching motivated students or explaining some phenomena of higher complexity.

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