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QUANTUM CHEMICAL STUDY OF COMPLEXES OF 1,3,5-TRIS-(β-OXYETHYL) HEXAHYDRO-S-TRIAZINE WITH Cu(II) CATION

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Abstract. Quantum chemical calculations were carried out for the most stable conformational structure of the supramolecular chelate complex formed by the Cu^{2+} cation and 1,3,5-tris-(β-hydroxyethyl)hexahydro-s-triazine [L-ligand]. Calculation of the charge density distribution in a molecule from the optimized structure of organometallic complexes is based on semi-empirical (PM3), electrostatic potential, reactivity descriptors, stable energy values, density functional theory (DFT), Monti Carlo algorithm and the B3LYP/6-31G* basic set * considered supporting Plamini. Values for the HUMO and LUMO levels were obtained to facilitate access to molecular orbital energy calculations. Hirschfeld surface analysis was also performed to study the intermolecular interactions in the supramolecular complex formed by the Cu^{2+} cation and 1,3,5-tris-(β-hydroxyethyl)hexahydro-S-triazine.

Key words: supramolecular, chelate complex, quantum chemical calculation, DFT, Monti-Carlo algorithm, Hirschfeld surface analysis.

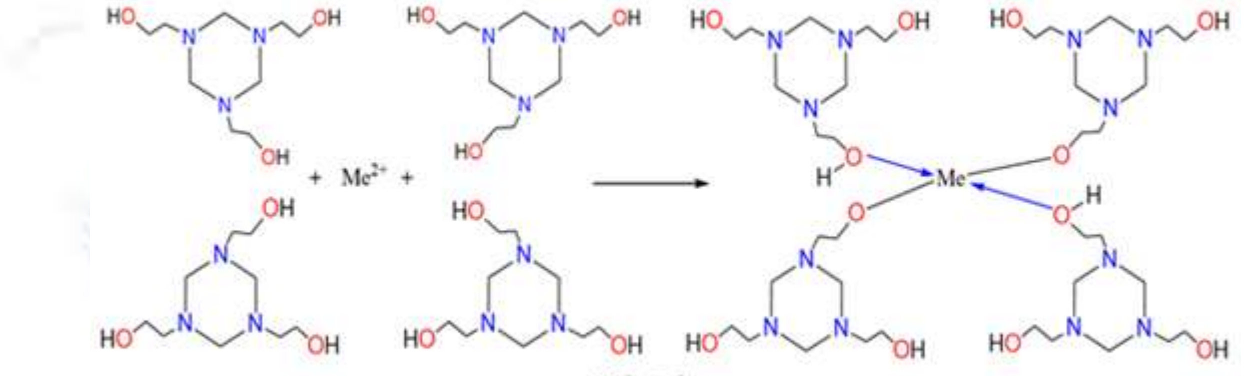
Introduction

In recent years, the synthesis of supramolecular structural complexes based on transition metal cations and organic ligands has been growing rapidly [1-3]. Among complexes of this type, 2D- or 3D-metal-supramolecular compounds formed by the mechanism of cooperative self-assembly, the areas of application of which are currently expanding, are of particular importance. In the synthesis of supramolecular metal compounds, organo-inorganic hybrid crystals, formed due to the coordination of metal ions and increasing the selectivity of substrate molecules as a result of non-covalent “guest-host” interactions, are optical and dielectric nanoporous materials with high adsorption capacity and are selective in photocatalytic reactions. Catalysts have unique physicochemical properties, such as high luminescence, ferroelectricity and ferromagnetism during phase transition [4-5].

Multidentate hybrid complexes obtained on the basis of Cu^{2+}, Ni^{2+} cations of various triazine derivatives as an organic ligand are also important in the preparation of adsorbents, transport bioactive substances and catalysts with high potential activity. Triazine-based ligands have a tridentate type of coordination, which allows them to form stable complexes with intermediate metal cations such as Cu^{2+}, Ni^{2+}. These types of stable supramolecular structural complexes can act as fluorescent or chromogenic probes that selectively bind to specific reagents and produce detectable signals [6–8].

Also, supramolecular complexes derived from [L] and Cu(II) cations can serve as carriers or drug delivery vehicles. Targeted and controlled drug release can be achieved by incorporating drug molecules into a complex structure or by attaching them to a ligand. In materials science, the self-assembly properties of Cu(II) complexes based on triazine derivatives make them important in the field of materials science [9–10]. These complexes enable the preparation of new types of materials with supramolecular systems, such as coordination polymers or metal-organic hybrid materials, used in areas such as gas storage, catalysis and optoelectronic devices. Therefore, in this work, the formation of a supramolecular complex of 1,3,5-tris-(β-hydroxyethyl)hexahydro-S-triazine with Cu^{2+} and Ni^{2+} cations was carried out using the Gaussian 09 and HyperChem programs.

Results and its discussion. The formation reaction of a chelate complex from Cu^{2+} and Ni^{2+} cations with 1,3,5-tris-(β-hydroxyethyl)hexahydro-S-triazine is as follows:



Me^{2+}: Cu^{2+},

From the reaction scheme, the formation of coordination bonds between Me-L (Me:Cu2+) and –Me-OH was determined by the formation of HL bonds between the ligands. During the synthesis of complexes, the dispersion effect (ED) and electronic correlation (EC) have the greatest influence on the formation of the molecular structure and the formation of coordination bonds. Dispersion forces for planar triazine-type ligands in organometallic chelate molecules are relatively small for singlet spin states. However, the calculated dispersion effects for triazine ligands and metal cations were higher. This occurs due to the formation of coordination bonds due to the high electrostatic potential of the metal ion and the negatively charged axial ligand. This interaction, in turn, significantly increases the stability of the resulting octahedral structure. In fig.1 shows the octahedral structure of the complexes formed by the Cu(II) cation and the 1,3,5-tris-(β-oxyethyl)hexahydro-S-triazine ligand, calculated using the Gaussian 09 software package on the basis set DFT/B3LYP/6-31G **(p, d).

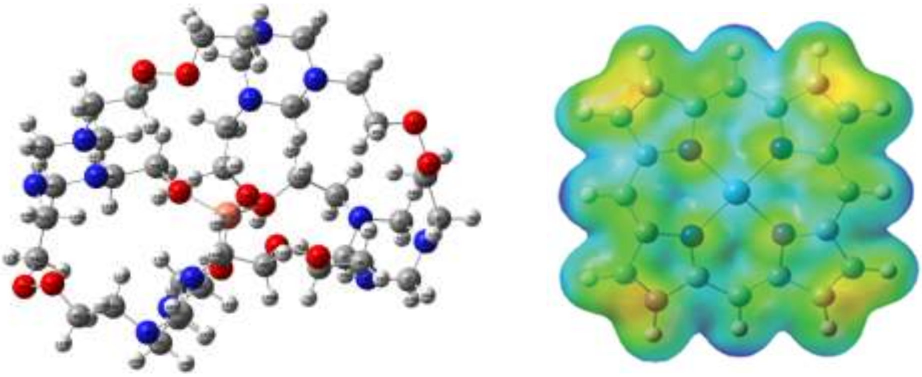


Figure 1. Molecular structure of the resulting complex and charge distribution in the complex.

Optimization of modeled monodentate complexes and calculation of their molecular parameters were carried out using quantum chemical methods (semi-empirical PM3 and DFT/B3LYP/6-31G**(p, d)). Geometric and molecular parameters were calculated by both methods and the results obtained were compared with reference data on the bonds formed between atoms and groups of atoms (Table 1).

Table 1.

Geometric parameters of complex Cu(II)-L, calculated by semi-empirical (PM3) and DFT (B3LYP/6-31G(d, p)) method.

Химические связи	**Стандарт [14]**	**PM3**	**DFT**	**Ab initio**
Длина связи (A°)				
Cu-6O	2.328	1.840 (0.488)	1.773 (0.555)	2.197 (0.131)
Cu-14O	2.375	2.007 (0.368)	2.105 (0.270)	2.265 (0.110)
8O-10H	2.007	1.877 (0.130)	1.874 (0.133)	1.922 (0.085)
10O-14H	2.042	1.898 (0.106)	1.868 (0.136)	1.998 (0.044)
Угол связи (°)				
Cu-6O	80.27	86.75 (-6.48)	86.34 (-6.07)	84.12 (-3.85)
Cu-14O	173.87	169.61 (-74.34)	172.32 (1.55)	171.79 (2.08)
8O-10H	89.51	100.38 (-10.87)	99.71 (-10.20)	94.06 (-4.55)
10O-14H	172.23	176.28 (-4.05)	172.00 (0.23)	173.18 (0.95)

The table shows that the bond distances (A°) calculated by PM3, DFT and Ab initio methods for Cu-6O are respectively 1.840 Å; 1.773 Å; 2.197 Å; and for Cu-14O 2.007 A°; 2.265 A°; 2.105 A°.

Table 2 presents the geometric parameters of the complex formed from the Ni(II) cation and 1,3,5-tris-(beta-oxyethyl)hexahydro-s-triazine.

Table 2

Geometric parameters of the Ni(II)-L complex calculated by semi-empirical (PM3) and DFT ((B3LYP/6-31G(d, p)) methods.

Химические связи	**Стандарт [14]**	**PM3**	**DFT**	**Ab initio**
Длина связи (A°)				
Ni-6O	1.994	2.005 (-0.011)	2.131 (-0.137)	1.921 (0.073)

Ni-14O	1.995	1.927 (0.068)	1.771 (0.224)	1.957 (0.038)
8O-10H	2.007	1.877 (0.130)	1.874 (0.133)	1.922 (0.085)
10O-14H	2.042	1.898 (0.106)	1.868 (0.136)	1.998 (0.044)
Угол связи (°)				
Ni-6O	85.27	78.35 (6.92)	101.79 (-16.52)	88.82 (-3.55)
Ni-14O	90.24	80.49 (9.75)	79.52 (10.72)	86.54 (3.70)
8O-10H	89.51	100.38 (-10.87)	99.71 (-10.20)	94.06 (-4.55)
10O-14H	172.23	176.28 (-4.05)	172.00 (0.23)	173.18 (0.95)

The distance between coordination bonds of Ni-6O and Ni-14O is calculated to be 2.005 Å°, 2.131 Å°, 1.921 Å° and 1.927 Å°, 1.771 Å°, 1.957 Å°, respectively. In general, it can be seen that the bond lengths obtained by the DFT method are closer to the experimental results than the values obtained by the semi-empirical method.

The highest occupied molecular orbital (HUMO) and the lowest unoccupied molecular orbital (LUMO) are called frontier molecular orbitals (FMO). FMOs play an important role in optical and electrical properties as well as quantum chemistry [12]. HUMO represents the ability to donate an electron to an electron-deficient molecule, which is also related to ionization potential. The ability of a ligand to bind to a metal increases with increasing HUMO energy value. LUMO as the ability to accept an electron (i.e. related to electron affinity), which also provides information about the electron affinity of the compound [11].

FMO plots obtained in Gaussian 09 show that the HUMO and LUMO of the chelate complex formed with Cu(II) and the ligand are presented in Fig. 2.

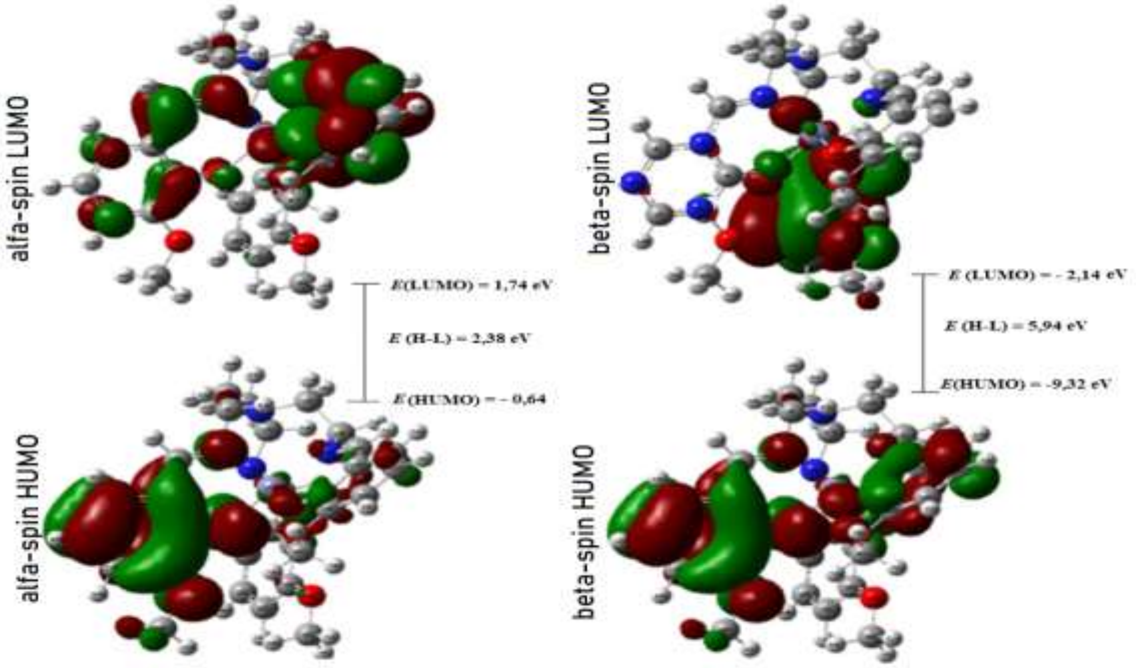


Figure 2. Energy distribution of HUMO and LUMO in the MO complex of Cu(II) with 1,3,5-tris-(β-oxyethyl)hexahydro-S-triazine

The FMO energies (EHUMO, ELUMO and EHUMO-LUMO) calculated for the Cu(II) complex with 1,3,5-tris-(β-oxyethyl)hexahydro-S-triazine by semi-empirical and DFT methods are, respectively:

-8.77 , -3.85, 4.92 eV and -8.08, -3.23, 5.45. It is seen to be −0.75, 1.42, and 2.17 eV for PM3, PM6, and DFT, respectively. Also, using the Gaussian 09 software package, calculations were carried out using the PM3, Ab initio and DFT/B3LYP/6-31G**(p, d) methods to determine the geometry of chelate complexes, electrophilicity/nucleophilicity (ō), chemical potential (μ) and chemical stability (ƞ). Based on the data obtained, the structure of the molecules and their reactivity were assessed. It is known that the electrophilicity of ligands can be calculated based on the relationship: ō = m2/2ƞ. This geometric parameter measures the stability of energy when charging an additional electron.

It can be seen that the FMO energies (EHOMO, ELUMO and EHOMO-LUMO) calculated for the Ni(II)-L complex by the DFT method are -8.77 and 5.45 eV, and for PM3 -0.75 and 2.17 eV .

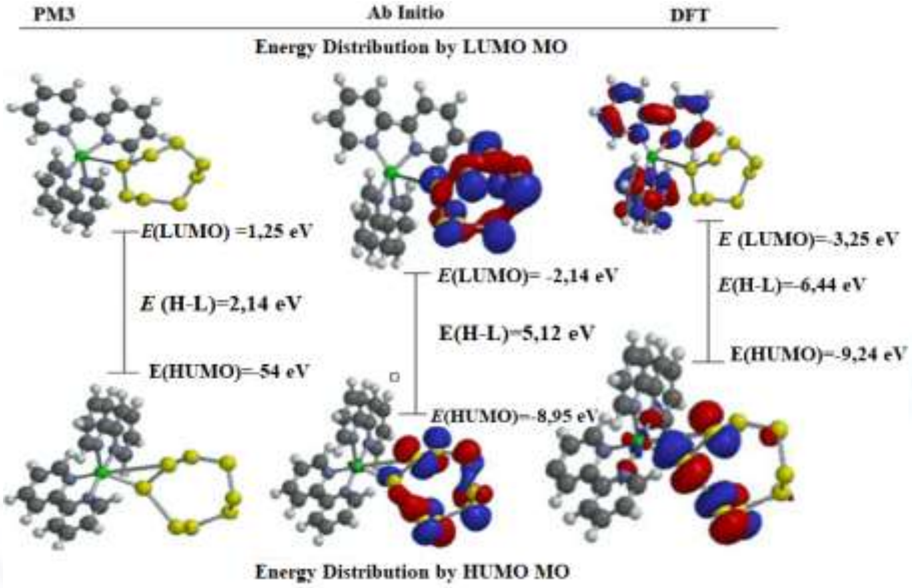


Figure 3. Energy distribution of HUMO and LUMO across MOs of Cu(II)-L and Ni(II)-L complexes

The energy gap of the Cu(II)-L complex, calculated by the DFT method, turned out to be narrower and thermodynamically stable than that of the Ni(II) complex.

Electrophilicity includes the ability of an electrophile to acquire additional electronic charge and the stability of the system to exchange electronic charge with the environment. However, studies have shown that the electrophilicity/nucleophilicity index is a very useful structural descriptor for assessing the reactivity of molecules [16]. Therefore, the chemical potential and chemical stability using FMO energies can be expressed as follows: m=1/2 (EHUMO + ELUMO) and ƞ=1/2 (-EHUMO + ELUMO) [17-18]. The chemical potential values calculated by DFT, PM3 and Ab initio methods are -0.335/-0.330, -6.31/-6.495 and -5.655/-6.050 eV, respectively, for the complex derived from the triazine derivative with Cu(II). Chemical activity is characterized by electrophilic potential and a high value of chemical potential (μ), which has the ability to gain additional electronic charge, which, in turn, better describes chemical reactivity [17-20]. Therefore, using the PM3, Ab initio and DFT/B3LYP/6-31G**(p, d) methods, we calculated the geometric parameters, chemical potential (μ), dipole moment, electrophilicity (σ), chemical stability and total energy of the complex, the results of which is shown in table 3.

Table 3

Geometric parameters of Cu(II)-L and Ni(II)-L complexes

	Дипольный момент (Дэбай)	*μ* (eV)	ƞ (eV)	σ (eV)	*E* (*a.u*)	*S.E* (ккал/моль)
Комплекс Cu(II)-L						
DFT	6,56±0,14	-3,345±0,95	1,08±0,23	0,462±0,01	-418,546	-5,62·10^2
PM3	3,80±0,48	-5,816±0,19	2,460±0,14	0,206±0,04	-305,72	-3,52·10^2
Ab I	6,44±0,45	-10,44±0,45	2,425±0,34	0,186±0,09	-226,46	-1,18·10^2
Комплекс Ni (II)-L						
DFT	5,77±0,54	-2,565±0,38	0,996±0,56	0,513±0,05	-614,37	-8,46·10^2
PM3	2,31±0,65	-6,420±0,84	2,550±0,31	0,196±0,05	-284,12	-6,20·10^2
Ab I	5,56±0,18	-8,48±0,23	2,88±0,86	0,173±0,07	-210,29	-2,14·10^2

The total energy of the [CuL] complex calculated by the DFT method is E = -418.546 a.u., and the dipole moment is 6.56 ± 0.14 deby. The values of the geometric parameters of the complex obtained as a result of different quantum chemical calculations partially differ from each other. To visually represent the dependence of the total energy of the Cu(II)-L and Ni(II)-L complexes with their dipole moment and chemical potential, you can use a three-dimensional diagram, where each axis will correspond to one of the parameters: dipole moment (μ), chemical potential (Ƞ) and total energy (E). For convenience, we can use normalized parameter values to range from 0 to 1. Thus, the X-axis can represent the dipole moment (μ), the Y-axis the chemical potential (Ƞ), and the Z-axis the total energy (E). Data points for each complex can be shown in this three-dimensional coordinate system (see Fig. 4).

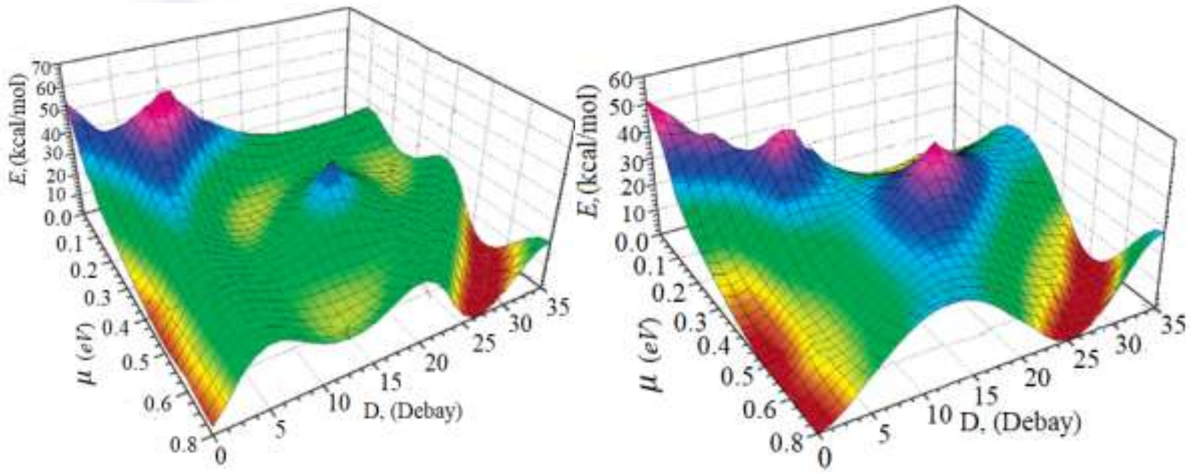


Figure 4. Values of surface potential energy in complexes of Cu(II) (a) and Ni(II) (b) ions with triazine, calculated in the Gaussian program

The graph will allow you to clearly see the relationship between the dipole moment, chemical potential and total energy of the complexes. For example, you can notice that as the dipole moment increases, the total energy of the complex can change in a certain direction. You can also pay attention to possible correlations or inverse relationships between the chemical potential and the total energy of the complexes.

It is important to remember that the accuracy and reliability of the data obtained depends on the calculation methods used (e.g. DFT, PM3, Ab initio). Also, standard deviations (shown in the table) can indicate uncertainty or variability in these parameters.

Representing the data in a 3D diagram will help researchers and chemists visualize and analyze the dependence of the total energy of complexes on their dipole moment and chemical potential in order to obtain new scientific research and discoveries. Also, using the Crystal Explorer 17.5 program, the nature of intermolecular interactions in the supramolecular structural complex formed between the ligand and the Cu(II) cation was studied based on the analysis of the Hirschfeld surface, complex non-covalent interactions (Fig. 5).

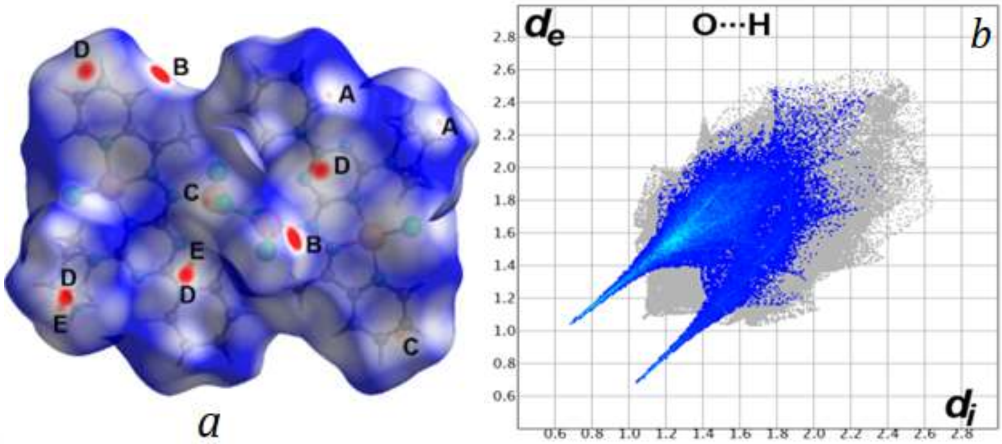


Figure 5. Hirschfeld surface and Hirschfeld fingerprints of Cu(II) complex with 1,3,5-tris-(β-hydroxyethyl)hexahydro-s-triazine

From Figure 5 it can be seen that there are red spots (α) on map b (norms). These red spots are associated with regions involved in short non-covalent interactions with neighboring molecules. It has been established that the most important non-covalent interactions are formed between the Cu....O and O....H atoms. Based on 2D Hirschfeld fingerprints, (b) non-covalent interactions between Cu....O atoms are 64.8% (blue areas in photo), while non-covalent interactions between O....H atoms were found to be 8.8 % (light areas in the figure).

IR spectra of the Cu(II) complex were also obtained by DFT using the Gaussian 09 program (Fig. 6a). The high-intensity peaks formed in the IR spectrum of the complex in the region of 1600-100 cm-1 are due to the stretching vibration of C-H bonds in 1,3,5-tris-(β-oxyethyl)hexahydro-S-triazine, and the peaks in the region of 3600-3300 cm-1 are caused by the stretching vibration of OH groups, which is formed due to vibrations. The presence of peaks in the range of 900-600 cm-1 in the spectra was established, caused by bending vibrations of Cu-O bonds formed due to Cu^{2+} cations and OH- groups. The calculated IR spectra were compared with the IR spectra of the synthesized complexes. IR spectra of the samples were obtained in the range of 600-3900 cm-1 using Fourier transform IR spectrometry (Bruker Tensor 27). During the analysis, the composite mixture was prepared as follows: 95% KBr and 5% sample. The IR spectrum of the sample is shown in Figure 6(b).

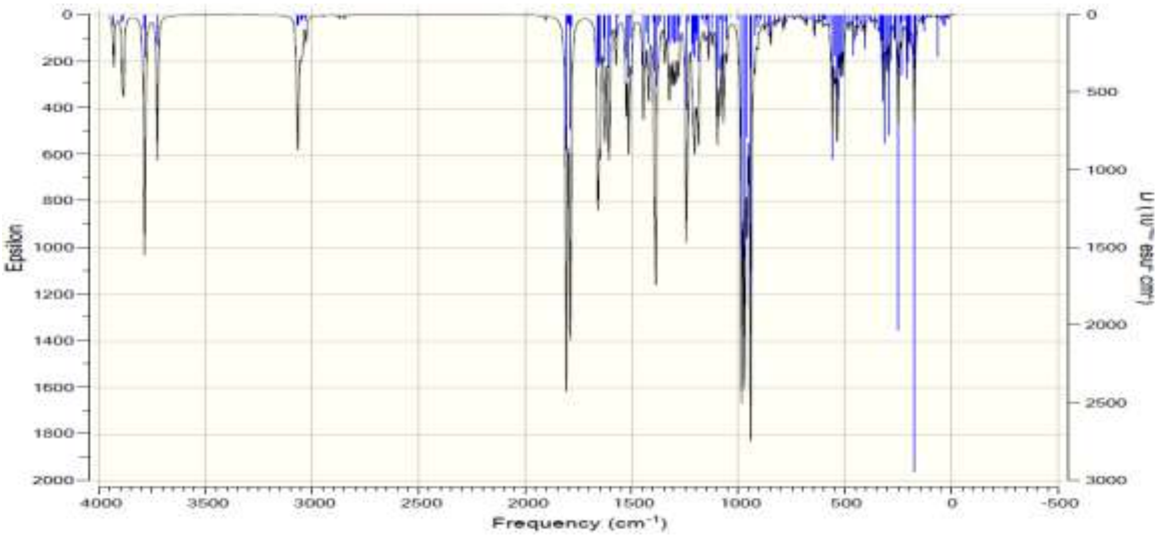


Figure 6(a). IR spectra of the complex obtained using the Gaussian 09 program

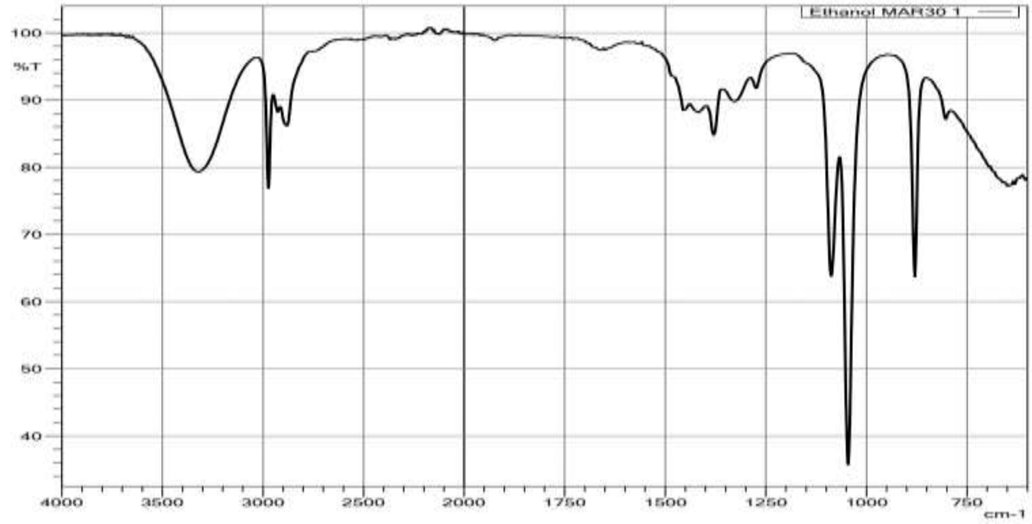


Figure 6(b). Experimental IR spectra of the complex

The degree of agreement of the IR spectra calculated by quantum chemical calculations with the experimentally obtained IR spectra was assessed by finding the correlation coefficients (Fig. 7).

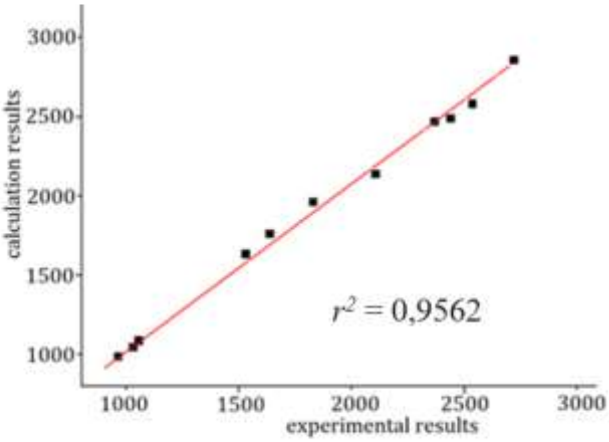


Figure 7. Degree of agreement between calculated and experimental IR spectra

The degree of agreement between the calculated and experimental IR spectra was $r^2 = 0.9562$.

Thus, in this work, the structural stability of microcrystalline complexes formed by Cu(II) cations with the organic ligand 1,3,5 tris-(β-oxyethyl)hexahydro-S-triazine, charge transfer effects, and the state of reaction centers through electron density were studied. The distribution of atoms in a molecule, physical quantities such as the distance between them, were studied by the DFT method (B3LYP and CAM-B3LYP). According to the calculation results, the electrophilicity index of the complex (σ) is 0.462±0.01 eV; chemical potential (μ), -3.345±0.95 eV; and the total energy of the molecule is E=−418.546 a.u. The contribution of non-covalent interactions involved in complex formation is studied based on Hirschfeld surface analysis. According to which non-covalent interactions between Cu....O atoms account for 64.8%, O....H - 8.8%. It was also found that the degree of agreement between the synthesized complex IR spectra and the spectra obtained as a result of theoretical calculations using the Gaussian09 program is $r^2 = 0.9562$.

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