

QUANTUM CHEMICAL STUDY OF THE SYNTHESIS OF A CHILATE COMPLEX BASED ON Ni (II) CATION AND 1,3,5-TRIS-(BETTA OXOETHYL)HEXAHYDROOXO-S-TRIAZINE

¹Xodjayorova G.R., ²Ergashov Sh., ³Uzoqov J.R., ⁴Boboyorova N.S.

^{1,2,3,4}Samarkand State University named after Sharof Rashidov

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Abstract. Structural stability of microcrystalline complexes of some transition metal cations with organic ligand 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine, charge transfer effects, state of reaction centers through electron density distribution in the molecule, physical quantities such as distance between atoms were studied by DFT (B3LYP and CAM-B3LYP) method. Ni²⁺ cation and two: different 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine-based four-coordination octahedral metal-organic complexes with singlet and triplet spin states spin- was performed by calculating orbital bonds. According to it, the corresponding stability constant of the complexes formed by 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine with Ni (II) cations is $\log b = 4.56$, dipole moment (D, Debye) -6.125; total energy of the molecule (E .a.u) -418,546; -614.37 electrophilicity (s) was found to be 0.462 ± 0.01 eV.

Keywords: chelate complex, stability constant, dipole moment, reactivity, surface potential energy, IR spectrum.

I. Introduction

In recent years, the synthesis of supramolecular structural complexes based on cations of transition metals and organic ligands has increased dramatically [1-3]. Among this type of complexes, 2D or 3D metal-supramolecular compounds formed through the mechanism of cooperative self-assembly are particularly important, and now their fields of application are increasing [4]. In the synthesis of metal supramolecular compounds, organo-inorganic hybrid crystals formed by coordinating metal ions in non-covalent interactions between the "guest-host", increasing the selectivity of substrate molecules are optical and dielectric, nanoporous materials with high adsorption capacity, selective in photocatalytic reactions. catalysts, xylate complexes with unique physicochemical properties such as high luminescence, ferroelectricity and ferromagnetism during phase change were obtained [5-6].

The use of quantum chemical methods in the synthesis of complexes with predetermined properties, as well as molecular modeling and design of the synthesis process based on these methods is widely used. Quantum chemical methods can also be used to optimize conditions for the synthesis of complex compounds. Calculations help determine optimal reaction conditions, select appropriate solvents and catalysts, and predict possible side reactions [7-10].

In the synthesis of organic-inorganic hybrid supramolecular complexes, 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine, which is considered a s-triazine derivative, is of practical importance [11-14]. Tris-(beta-oxoethyl) hexahydrooxo-s-triazine is a tridentate ligand whose core consists of a hexahydrooxo-s-triazine ring with three beta-oxoethyl groups attached to it. In this structure, nitrogen atoms of triazine ring and oxygen atoms of 3 beta-oxoethyl groups in side chains can serve as coordination centers through unshared electron pairs. When forming a complex of 1,3,5-tris-(beta-oxoethyl) hexahydrooxo-S-triazine with a metal, the ligands can bind to the

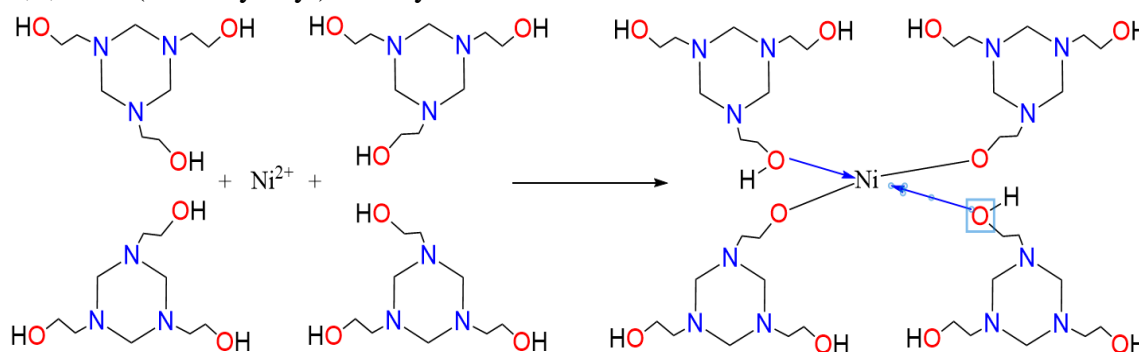
metal in a "host-guest" manner and form a sphere around the metal ion. The number and type of coordination bonds depends on the chemical nature of the metal and the structure of the complex. Such complexes can have different properties and are widely used in various fields, such as catalysis, photochemistry, medicine, and other fields [15].

The study of the literature showed that the synthesis of chelate complexes based on 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine and some transition metals, their stability and physicochemical properties have been little studied. In this work, complexes based on 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine and Ni(II) cation were prepared in an acidic medium and their properties were studied.

Calculation methods. Quantum chemical calculations were performed on the most stable conformational structure of the supramolecular xylate complex formed from Ni (II) cation and 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine. Calculation of the distribution of charge density in the molecule according to the optimized structure of metal-organic complexes is based on half-empiric (PM3), electrostatic potential, reactivity descriptors, stable energy values, density functional theory (DFT), Monte-Carlo algorithm and B3LYP/6-31G** basis set. implemented using plamini. The values of the HUMO and LUMO levels were obtained for easy access to calculations of molecular orbital energies. All quantum chemical calculations were performed using Gaussian 09 and HyperChem software on an Intel Core (TM) i3-2350 M processor, 1.68 GHz computer.

Results and their discussion.

According to the reaction scheme for the formation of xylate complexes from Ni²⁺ cations and 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine.



From the reaction scheme, it can be seen that the formation of coordination bonds between Me-L (Me: Ni²⁺) occurs at the expense of oxygen atoms in beta-oxoethyl groups of 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine. In the synthesis of complexes, the dispersion effect (DE) and electron correlation (EC) have the greatest influence on the formation of the molecular structure and the formation of coordination bonds. Dispersion forces for triazine-type planar ligands in metal-organic chelate molecules are relatively weak for singlet spin states. However, the calculated dispersion effects for triazine ligands and metal cations were found to be higher. The reason for this is 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. Figure 1 shows the octahedral structure of the complex formed by Ni (II) and 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine, DFT/B3LYP/6-31G**(p,d) basis in Gaussian 09 program the state calculated using the set is presented [16-18]. From the picture, it is possible to see coordination bonds formed by oxygen atoms in beta-oxoethyl groups of Ni (II) and 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine. In the structure of the

complex, strong bonds are formed due to the strong interaction between the negatively charged axial ligand and the metal ion. The energy of these bonds was determined to be 34,62 kcal/mol when calculated by the DFT/B3LYP/6-31G** method. The distance between Ni-O bonds was calculated to be $1,875 \div 1,976 \text{ \AA}$.

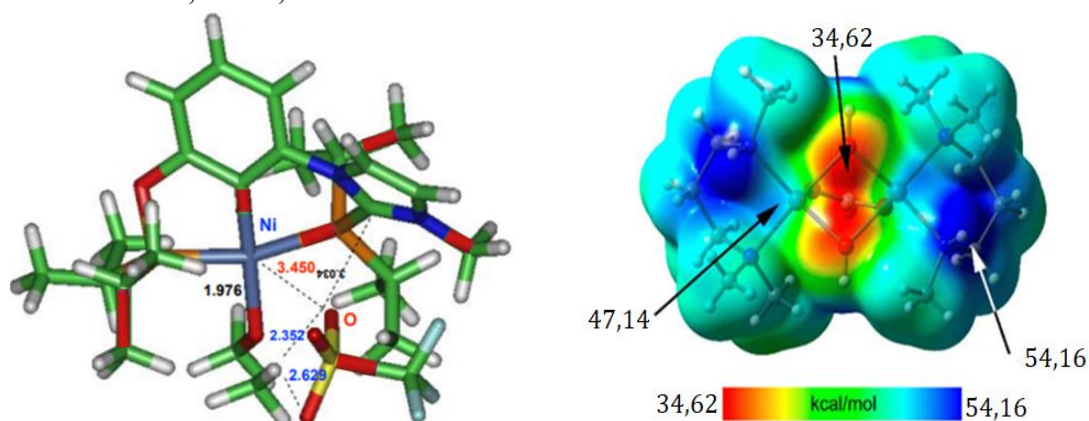


Figure 1. Distribution of electrostatic potential charge around triazine-type ligand and Ni (II) complex

Optimization of modeled monodentate complexes and calculation of molecular parameters was carried out using quantum chemical methods (semi-empirical PM3, empirical Ab initio and DFT/B3LYP/6-31G**(p,d)). Geometrical and molecular parameters were calculated by all three methods and the obtained results were compared with the standard of bonds formed between atoms and groups of atoms (Table 1).

Table 1

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

Chemical gardens	Standard [119]	PM3	DFT	Ab initio
Bond length (\AA)				
Ni-O	1.876	$2,134 \pm 0,02$	$1,976 \pm 0,04$	$2,005 \pm 0,02$
Bond angle ($^\circ$)				
Ni-O	85.27	78.35 (6.92)	101.79 (-16.52)	88.82 (-3.55)

From the table, the distance between coordination bonds formed between Ni-O is 2.134 \AA in PM3; empirically. 2.005 \AA in the ab initio method; and showed that it consists of 1.976 \AA by the DFT method. It can be shown that the values of the bond lengths obtained by the DFT method are closer to the values obtained by the experimental method than the values obtained by the semi-empirical method.

The highest occupied molecular orbital (HOMO) 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 in quantum chemistry. HOMO represents the ability to donate an electron to an electron-deficient molecule; which is also related to the ionization potential. The ability of a ligand to bind to a metal increase with increasing HOMO energy values. LUMO as the ability to accept an electron (i.e. related to electron affinity; the ability to accept an electron from an electron-rich molecule), which also provides information about the electron affinity of a compound.

DFT/B3LYP/6-31G**(p,d) method in Gaussian 09 program of the xylate complex formed by Ni (II) with 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine (frontier molecular orbitals) graph of FMO is presented in Fig 2. From the figure, the highest occupied molecular orbitals in complexes based on Ni (II) show the possibilities of coordination bond formation. In the complex formed from Ni (II) and the ligand, it was calculated that the HUMO energy $E = -4.819$ eV and the LUMO orbitals with energy $E = -1.415$ eV have an energy of at least 3.404 eV. It is possible to observe the localization of s-triazine type ligands due to unshared electron pairs of oxygen and nitrogen atoms.

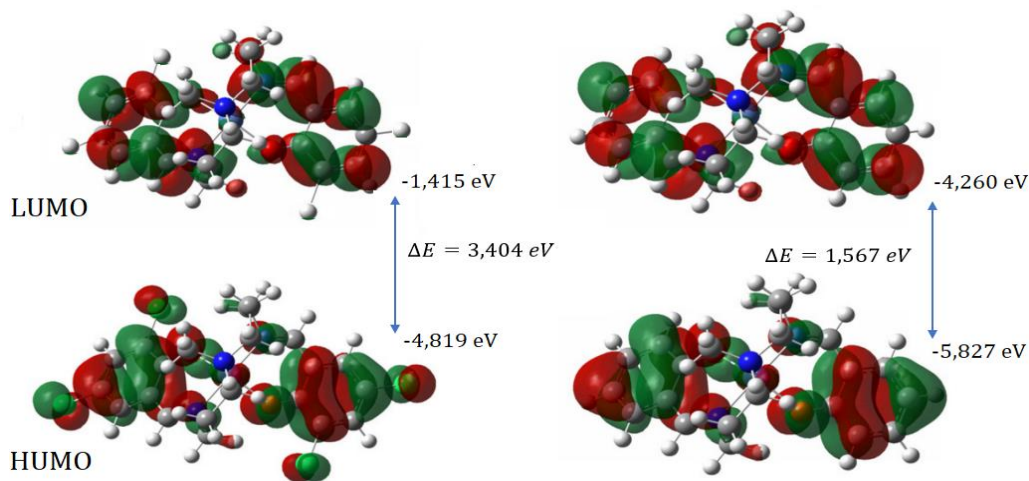


Figure 2. HUMO and LUMO orbitals of triazine-type ligand and Ni(II) complex

Also, by using the DFT/B3LYP/6-31G**(p,d) method using the Gaussian 09 software, the structure of molecules and their reactivity was evaluated. Based on the molecular structure of the complex, it is possible to calculate the chemical stability (η) of the complex based on electron affinity (A), ionization potential (I) and HUMO and LUMO energies:

$$\eta = (I - A) = (E_{LUMO} - E_{HUMO})/2$$

As the HOMO-LUMO energy difference increases, the relative chemical stability of the complex increases, but the reactivity decreases. The chemical potential of the complex directly depends on the electronegativity of the atoms in it and can be calculated using the following equation.

$$\mu = -\chi = -(I - A)/2$$

An increase in the value of the chemical potential increases the reactivity of the complex. Similarly, the electrophilic index of a complex can be calculated based on chemical stability, chemical potential, and electronegativity.

$$\omega = (\mu^2/2\eta) = (-\chi^2)/2\eta$$

Also, the nature of intermolecular interactions, complex non-covalent interactions based on Hirschfeld surface analysis in the supramolecular structural complex formed between s-triazine and Ni (II) cation CrystalExplorer 17.5 software was studied using (Fig. 3).

It can be seen from the figure that there are some red spots (a) on the d(norm) map. These red spots are associated with regions involved in short non-covalent interactions with neighboring molecules. It was found that the most important non-covalent interactions occurred between Ni...O and O...H atoms. From the two-dimensional Hirschfeld fingerprints, (b) Ni...O non-covalent interactions account for 64.8% (pictured; blue regions), while non-covalent interactions between O...H atoms interactions were found to account for 8.8% (in the figure; light colored regions)

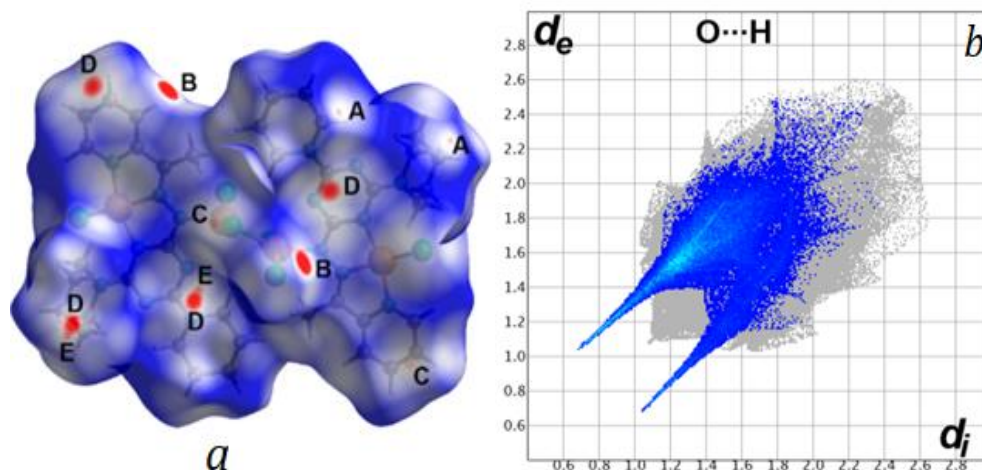


Figure 3. Hirschfeld surfaces and Hirschfeld fingerprints of complexes derived from Ni(II) and 1,3,5-tris-(beta oxyethyl)hexahydro-s-triazine

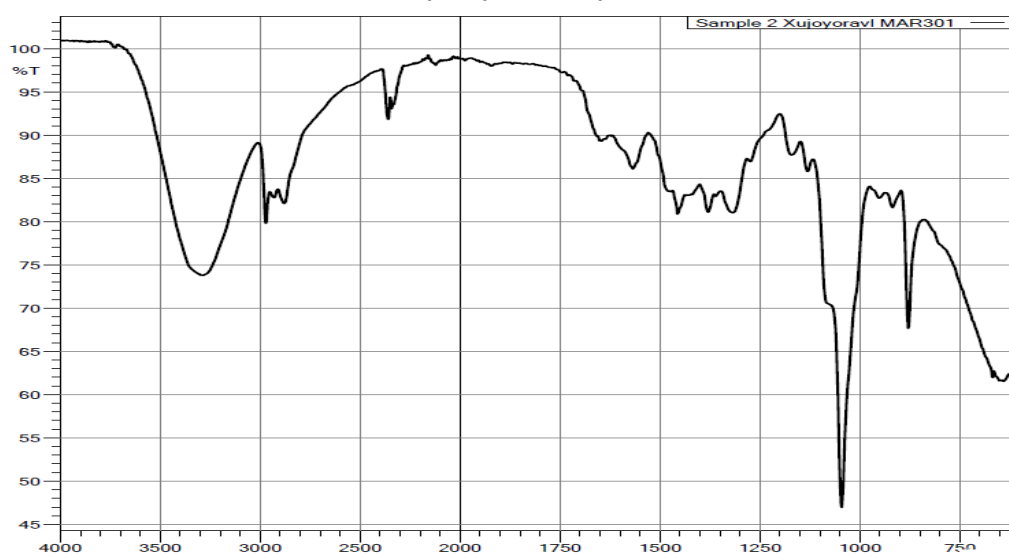


Figure 4. Experimental IR spectra of triazine derivative and complex obtained from Ni²⁺ cations

Also, IR spectra of the Ni (II) complex were obtained using the DFT method in the Gaussian 09 program (Fig. 5).

The high-intensity peaks formed in the IR spectrum of the complex in the 1600-100 cm⁻¹ range are due to the valence vibration of 1,3,5-tris-(beta oxyethyl) hexahydro-S-triazine C-H bonds, and the peaks in the 3600-3300 cm⁻¹ range are due to the valence vibration of OH groups it can be seen that they are formed due to vibrations.

It was determined that there are peaks at 900-600 cm⁻¹ of the spectra formed by the deformation vibration of Ni-O bonds formed at the expense of Ni²⁺ cations and OH groups. The obtained 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 Fure transform IR spectroscopy on a Bruker Tensor 27 instrument. During the analysis, the composition mixture was prepared as follows: 95% KBr and 5% sample mixture.

The degree of agreement between quantum chemical calculations and experimentally obtained IR spectra was evaluated by finding correlation coefficients by the method of short squares (Fig. 6).

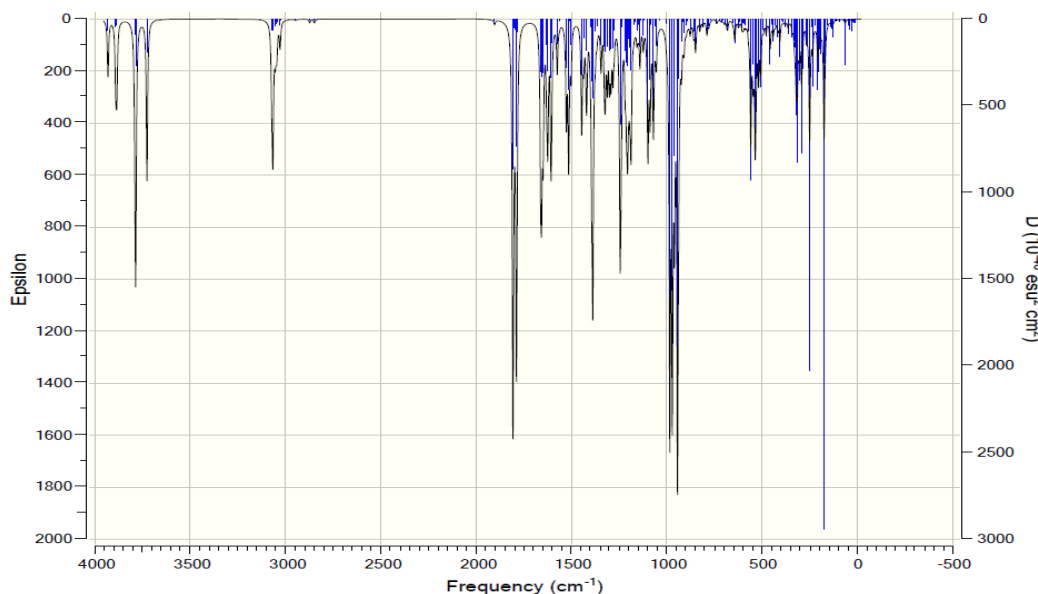


Figure 5. Calculated IR spectra of the triazine derivative and the complex obtained from Ni²⁺ cations

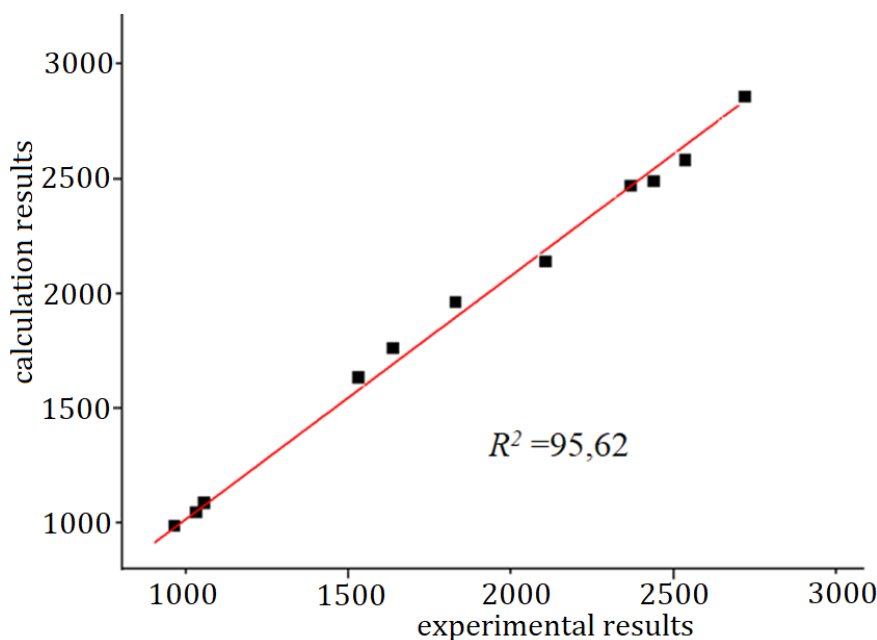


Figure 6. The degree of smoothness of the IR spectra obtained in the experiment and in the Gaussian 09 program.

The degree of agreement of IR spectra obtained in calculations and experiment was $R^2 = 0.9562$. In this work, structural stability of microcrystalline complexes of Ni (II) cations formed with organic ligand 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine, charge transfer effects, state of reaction centers through electron density distribution in the molecule, atoms physical quantities such as the distance between were studied by DFT (B3LYP and CAM-B3LYP) method. According to the calculation results, the electrophilic index of the complex (c) is $0,462 \pm 0.01\text{eV}$; chemical potential (m), $-3.345 \pm 0.95\text{ eV}$; and the total energy of the molecule is $E = -418,546\text{ a.u.}$ was found to be. Also, the corresponding stability constant of the complexes formed by 1,3,5-tris-(beta oxyethyl) hexahydro-s-triazine with Ni (II) cations is $\log b = 4.56$; $\log b = 5.14$ dipole moment (D, debay) was found to be 6,125 molecules.

The contribution of non-covalent interactions involved in complex formation was studied based on Hirschfeld surface analysis. According to it: Ni...O non-covalent interactions account for 64.8%, and O...H non-covalent interactions between atoms make 8.8% found. It was also found that the degree of agreement between the synthesized complex IR spectra and the spectra obtained from theoretical calculations using the Gaussian09 program is $R_2 = 0.9562$.

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