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КВАНТОВО-ХИМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ТИПА КООРДИНИРОВАНИЯ МАРГАНЦА С ВИТАМИНОМ B_2 И НЕЗАМЕНИМЫМИ АМИНОКИСЛОТАМИ

QUANTUM CHEMICAL MODELING OF THE TYPE OF COORDINATION OF MANGANESE WITH VITAMIN B2 AND ESSENTIAL AMINO ACIDS

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В рамках данного исследования проведено квантово-химическое моделирование типа координирования марганца с витамином B_2 и незаменимыми аминокислотами. Взаимодействие марганца с аминокислотами рассматривалось через карбоксильную группу и аминогруппу аминокислоты, с витамином B_2 – через различные пары енольного кислорода и соседнего гетероатома азота. В результате моделирования установлено, что все представленные взаимодействия являются энергетически выгодными ($\Delta E \geq 2331{,}756$ ккал/моль) и химически стабильными ($\eta \geq 0{,}096$ эВ). Координирование марганца с витамином B_2 и незаменимыми аминокислотами происходит через N_3 и енольный кислород, присоединённый к C_2 атому, в пиримидиновом кольце витамина B_2, и через карбоксильную группу и аминогруппу, присоединённую к C_2 атому углерода, аминокислот.

Ключевые слова: *витамин B_2, квантово-химическое моделирование, незаменимые аминокислоты, хелатные комплексы, марганец*

Abstract

Within the framework of this study, quantum chemical modeling of the type of coordination of manganese with vitamin B_2 and essential amino acids was carried out. The interaction of manganese with amino acids was carried out through the carboxyl group and amino group of the amino acid, interaction with vitamin B_2 was carried out through various pairs of enolic oxygen and a neighboring nitrogen heteroatom. As a result of modeling, it was found that all the presented interactions are energetically favorable ($\Delta E \geq 2331{,}756$ kcal/mol) and chemically stable ($\eta \geq 0.096$ eV). The coordination of manganese with vitamin B2 and essential amino acids occurs through N3 and enolic oxygen attached to the C2 atom in the pyrimidine ring of vitamin B2, and through the carboxyl group and amino group attached to the C2 atom of amino acids.

Key words: vitamin B_2, quantum chemical modeling, essential amino acids, chelate complexes, manganese

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Introduction

Nutrition is one of the key factors affecting human health, its performance and life expectancy. An urgent problem at the moment is the problem of microelement deficiency - lack of bioavailable essential trace elements that protect the body from the influence of negative factors and provide resistance to diseases [1]. These substances include vitamins, amino acids and various trace elements.

There are eight essential amino acids in total: isoleucine, leucine, valine, tryptophan, phenylalanine, lysine, threonine, methionine. Each of them is involved in various biochemical processes in the body. For example, isoleucine promotes the restoration of tissue cells, participates in the regulation of glucose and cholesterol in the blood serum, and affects muscle recovery after exercise [2]. Lysine, like isoleucine, is necessary to maintain the energy level of the body, for the absorption and transport of calcium to bone tissues, as well as for the functioning of the gallbladder and the human endocrine system [3]. Tryptophan is necessary for the synthesis of vitamin B_3, is a precursor for the synthesis of serotonin, and is also used for the complex therapy of the psychoverbal development of children [4]. Threonine prevents the accumulation of fats in the liver; it is also necessary for the synthesis of glycine and serine [5].

An insufficient amount of essential microelements in human nutrition adversely affects its development, physical and mental activity, reduces the body's resistance to the influence of negative factors and leads to the development of a number of alimentary-dependent diseases [6, 7]. According to statistics, in the Leningrad region there is a deficiency in soil, water and plants of such essential microelements as zinc, iodine, manganese and selenium [8–10].

Manganese is an essential trace element and plays one of the key roles in the functioning of the gonads: a low level of manganese reduces sperm motility in men and significantly reduces the chance of conception in women. The key action of manganese is in insulin metabolism. People with diabetes are deficient in manganese: the content of manganese in the blood of this category of people is below the normal level [11, 12]. An important role of manganese is manifested in its antioxidant properties. In brain tissues, manganese is the most important cofactor for most enzymes, an example of which is superoxide dismutase (SOD), a “bodyguard” enzyme that protects body cells from oxidation [13].

However, not every form of essential microelements has high bioavailability, and as a result, the development of forms of essential microelements with high bioavailability is an actual direction of modern science. Scientists have established that triple chelated organic forms of trace elements are bioavailable for the human body [14–16]. The purpose of this study is quantum chemical modeling of the type of coordination of manganese with vitamin B_2 and essential amino acids.

Experimental part

QChem software using the molecular editor - IQmol, using the following construction parameters: calculation - Energy, method - HF, basis - 6-31G, convergence - 5, force field - Ghemical.

Within the framework of quantum-chemical modeling of the interaction of vitamin B_2, essential trace elements and essential amino acids, the total energy of the system (E), the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest free molecular orbital (E_{LUMO}), the energy difference between the amino acid and the system were calculated interactions (ΔE), chemical hardness (η), calculated by the formula:

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \qquad (1)$$

Discussion of the results

To determine the type of coordination of manganese with vitamin B_2 and essential amino acids at the first stage of research, models of essential amino acids were considered, then the interaction of manganese with essential amino acids and vitamin B_2 was considered. Coordination of the manganese atom with amino acids was carried out through the amino group attached to the C_2 atom and the carboxyl group; with vitamin B_2 through various pairs of enol oxygen and the neighboring nitrogen heteroatom. The simulation results are presented in Table 1.

Table 1 - Results of computer quantum-chemical modeling

Amino acid	Type of interaction with vitamin B_2	E, kcal/mol	ΔE, kcal/mol	E_{HOMO}, eV	E_{LUMO}, eV	η, eV
1	2	3	4	5	6	7
Lysine	Amino acid	-496.481	-	-0.177	-0.024	0.077
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2960.315	2463.829	-0.293	0.034	0.164
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2960.533	2464.049	-0.219	0.053	0.136
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2960.128	2463.639	-0.233	0.031	0.132
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2960.363	2463.879	-0.190	-0.001	0.095
Valine	Amino acid	-402.112	-	-0.249	0.016	0.133
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2866.631	2464.518	-0.242	0.041	0.142
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2866.535	2464.418	-0.234	0.034	0.134
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2866.620	2464.508	-0.173	0.028	0.101
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2866.328	2464.208	-0.205	0.022	0.114
Leucine	Amino acid	-441.397	-	-0.260	0.006	0.133
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2905.344	2463.943	-0.250	0.042	0.146
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2905.222	2463.823	-0.242	0.034	0.138
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2905.450	2464.053	-0.244 _	0.058	0.151
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2905, 381	2463.983	-0.190 _	0.012	0.101
Isoleucine	Amino acid	-441.394	-	-0.247	0.018	0.133
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2905.708	2464.306	-0.246	0.044	0.145
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2905.955	2464.556	-0.239	-0.017	0.111
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2905.460	2464.066	-0.221	0.032	0.127
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2905.440	2464.046	-0.199	-0.002	0.099
Methionine	Amino acid	-800.251	-	-0.232	0.006	0.119
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3264.091	2463.839	-0, 250	0.037	0.144
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3263.990	2463.739	-0.219 _	0.054	0.137
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-3263.935	2463.679	-0.247	0.045	0.146
	Through N_1 and enol oxygen attached to	-	2463.589	-0.194	-	0.096

1	2	3	4	5	6	7
	C_2 atom in the pyrimidine ring	3263.848			0.002	
Threonine	Amino acid	-438.015	-	-0.248	0.006	0.127
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	- 2902.411	2464.395	-0.243 _	0.045	0.144
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-2902.283	2464.265	-0.228 _	0.044	0.136
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-2902.258	2464.235	-0.242 _	0.056	0.149
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	- 2901.109	2463.085	-0.323 _	0.042	0.183
Tryptophan	Amino acid	-554.424	-	-0.240	0.002	0.121
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3148,505	2594.076	-0.244 _	0.043	0.144
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3148.342	2593.916	-0.235 _	0.044	0.140
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-3148.575	2594.150	-0.187 _	0.047	0.117
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-3148.571	2594.146	-0.196 _	0.003	0,100
Phenylalanine	Amino acid	-685.684	-	-0.195	-0.035	0.080
	Through N_5 in the pyrazine ring and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3018.032	2332.346	-0.241 _	0.045	0.143
	Through N_3 and enol oxygen attached to the C_4 atom in the pyrimidine ring	-3017.445	2331.756	-0.230 _	0.017	0.124
	Through N_3 and enol oxygen attached to C_2 atom in the pyrimidine ring	-3017.862	2332.176	-0.186 _	0.062	0.124
	Through N_1 and enol oxygen attached to C_2 atom in the pyrimidine ring	-3017.834	2332.146	-0.219 _	-0.003	0.108

As a result of data analysis, it was found that the coordination of triple chelate complexes of manganese with vitamin B_2 and essential amino acids is possible, which is confirmed by the high values of the energy difference ($\Delta E \geq 2331.756$ kcal/mol) and chemical rigidity of all molecular systems ($\eta \geq 0.096$ eV).

The highest value of the energy difference (ΔE = 2594.150 kcal/mol) has a complex of manganese with tryptophan and vitamin B_2 , where the interaction of manganese with vitamin B_2 passes through N_3 and enol oxygen attached to the C_2 atom in the pyrimidine ring of the vitamin B_2 (Figure 1), and the highest value of chemical hardness (η = 0.183 eV) is a complex of manganese with threonine and vitamin B_2 , in which the interaction occurs through N_1 and enol oxygen attached to the C_2 atom in the pyrimidine ring (Figure 2).

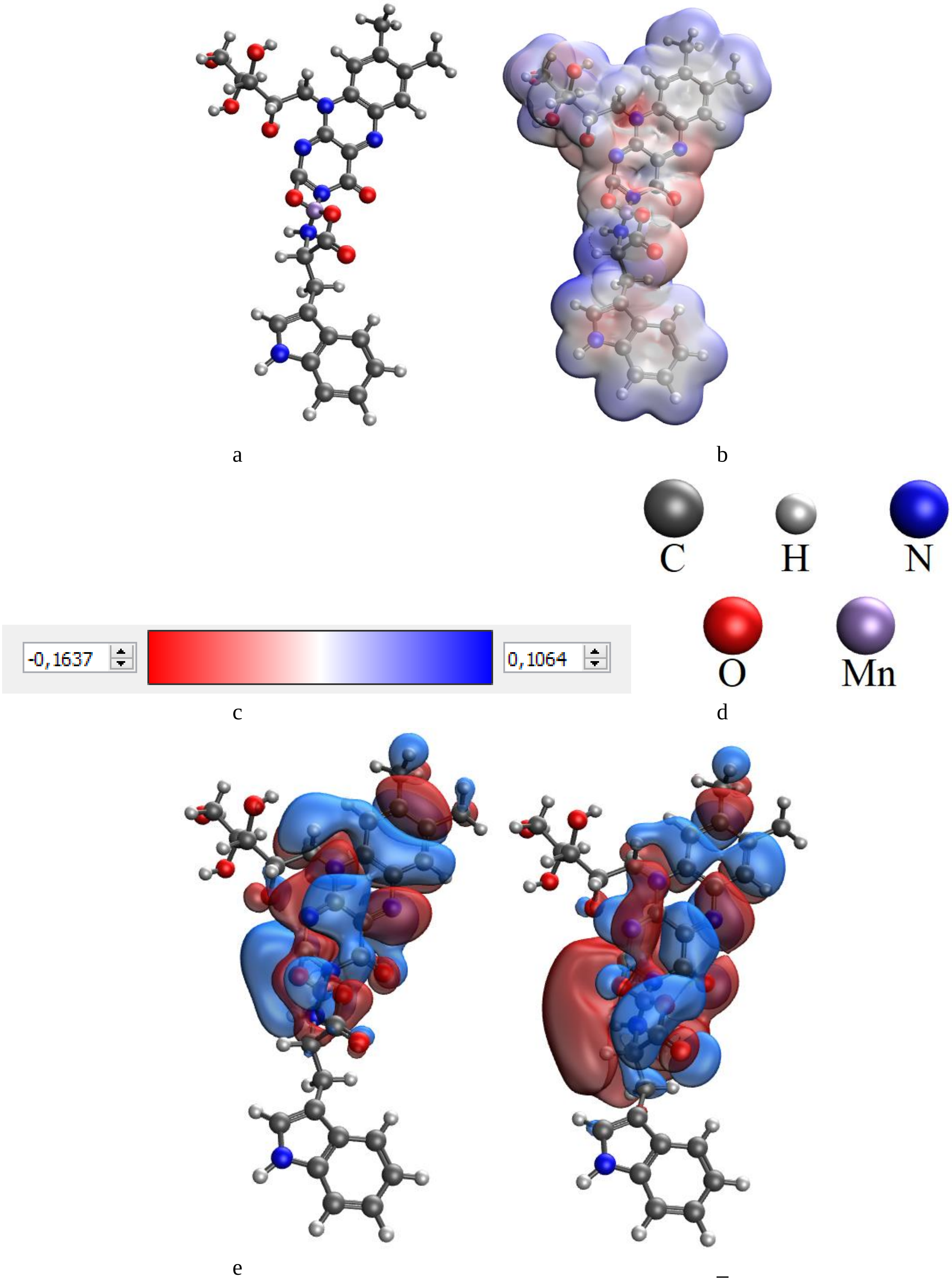

Figure 1 - The results of modeling the triple complex of tryptophan, vitamin B_2 and manganese, in which the interaction occurs through N_3 and enol oxygen attached to the C_2 atom in the pyrimidine ring of vitamin B_2: a – interaction model; b – electron density distribution; c – electron density distribution gradient; d – decoding; e – highest occupied molecular orbital *HOMO*; *e* – is the lowest free molecular orbital *LUMO*

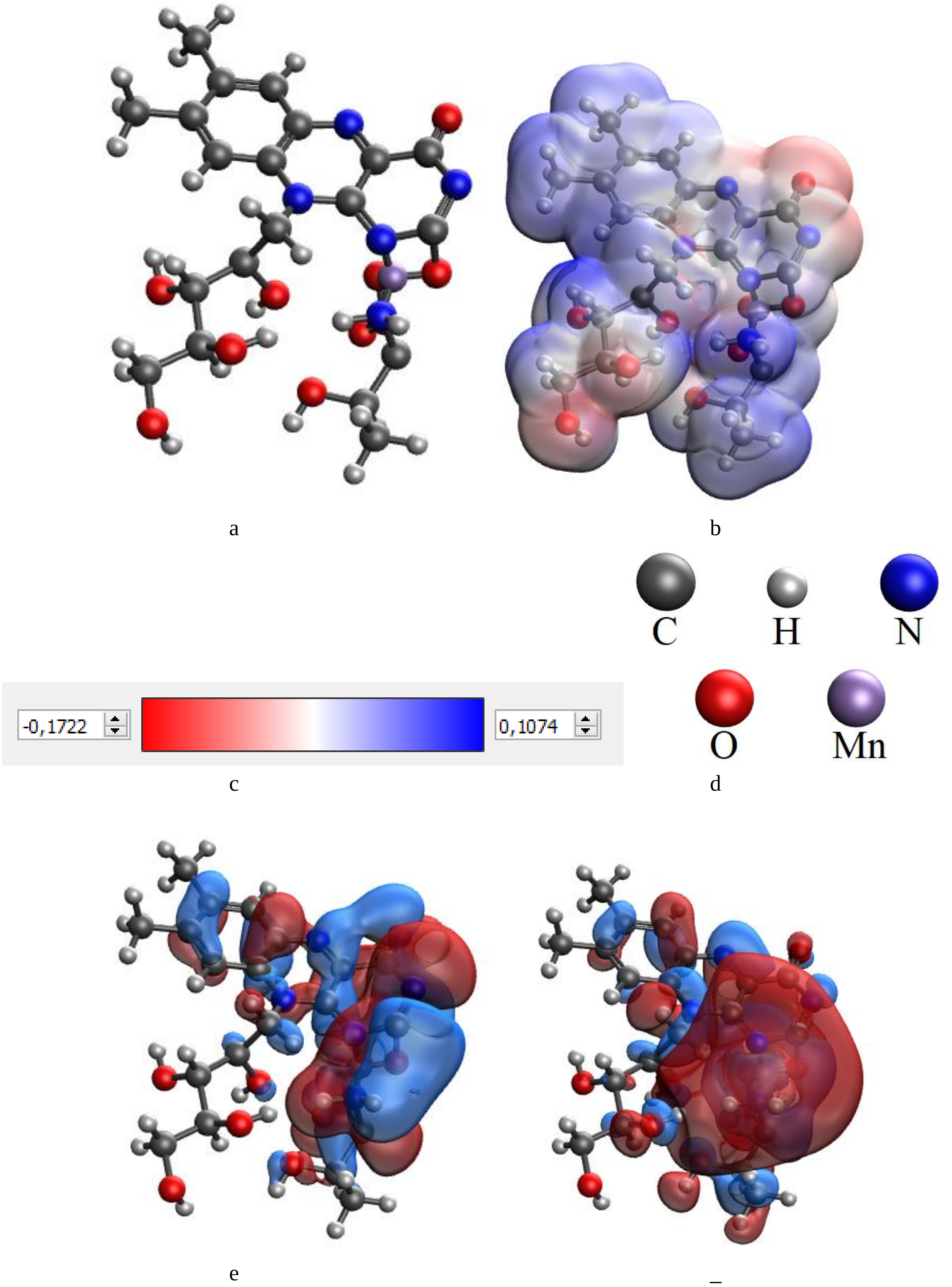

Figure 2 - The results of modeling the triple complex of threonine, vitamin B_2 and manganese, in which the interaction occurs through N_3 and enol oxygen attached to the C_2 atom in the pyrimidine ring of vitamin B_2: a – interaction model; b – electron density distribution; c – electron density distribution gradient; d – decoding; e – highest occupied molecular orbital *HOMO*; *e* – is the lowest free molecular orbital *LUMO*

The analysis of the obtained data established that the coordination of manganese with vitamin B_2 and essential amino acids occurs through N_3 and the enol oxygen attached to the C_2 atom in the pyrimidine ring of vitamin B_2, and through the carboxyl group and the amino group of the amino acids attached to C_1 and C_2 atoms.

Conclusion

As a result of quantum-chemical computer simulation, the possibility of coordination of triple chelate complexes of manganese with vitamin B_2 and essential amino acids was confirmed.

The obtained data on the total energy and chemical rigidity of the models allow us to conclude that the coordination of triple chelate complexes of manganese with vitamin B_2 and essential amino acids occurs through N_3 and enol oxygen attached to the C_2 atom in the pyrimidine ring.

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