

Electronic and molecular structure of M-DNA fragments

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Abstract To study M-DNA molecular structure (such DNA with transition metal ions placed between the nucleic bases is able to conduct the electric current) and its conductivity mechanisms, we carried out *ab initio* quantum-mechanical calculations of electronic and spatial structures, thermodynamic characteristics of adenine-thymine (AT) and guanine-cytosine (GC) base pair complexes with Zn^{2+} and Ni^{2+} . To take into account the influence of the alkaline environment, calculations for these complexes were also carried out with hydroxyl and two water molecules. Computations were performed at MP2 level of theory using 6–31+G* basis set. Analogous calculations were carried out for (AC)(TG) stacking dimer of nucleic acid base pairs with two Zn^{2+} . The calculation of the interaction energy in complexes has shown the preference of locating the metal ion (instead of the imino proton) between bases in M-DNA. The electronic transition energy calculation has revealed the reduction of the first singlet transition energy in AT and GC complexes with Ni^{2+} from 4.5 eV to 0.4–0.6 eV. Ni^{2+} orbitals take part in the formation of HOMO and LUMO on the complexes investigated. It was shown that charges of metal ions incorporated into complexes with nucleic bases and in dimer decrease significantly.

Keywords M-DNA · Metal ions · Molecular and electronic structures · MP2 level of theory calculation · Stacking dimer

Introduction

In the 1990s Canadian researchers revealed that ions of some bivalent metals (Ni^{2+} , Co^{2+} , Zn^{2+}) are able to be included in DNA base pairs [1]. Such a structure of DNA (M-DNA) was obtained experimentally in the alkaline environment at pH 8.5 [1–4]. NMR study of this structure has shown an absence of imino proton signals which allowed a supposition that in each base pair the imino proton is replaced by transition metal ion [1], and, thus, one-dimensional chain of transition metal ions is formed inside DNA macromolecule. X-ray studies of M-DNA have not been carried out. Direct investigations on conductivity of M-DNA placed between gold electrodes [2] showed that M-DNA is a better conductor of the electric current in comparison with DNA in B-form. A similar conclusion has been made on the basis of fluorometric study on the electron transport in synthetic oligonucleotides with the donor and acceptor attached to the polymer ends [1, 3].

The usage of M-DNA as a nanowire and a biosensor in nanotechnology [1–4] is being discussed. Recently works have been published [5, 6] in which molecular and electronic structures of the base pair of nucleic acids - guanine-cytosine (GC) - with Zn^{2+} , Co^{2+} , Fe^{2+} were determined at B3LYP/6–31G* level of calculations. The calculation of zone models of polynucleotide (polyG-polyC) with Zn^{2+} and Fe^{2+} has also been performed [6]. These works consider various models of GC pair with the transition metal ions and hydroxyl location in minor and major grooves of DNA macromolecule. Earlier we have presented reports about *ab initio* calculations of the

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electronic structure of adenine-uracil pair with Zn^{2+} as well as (AC)(TG) dimer and (ACA)(TGT) trimer of nucleic acid base pairs with zinc ions at MP2 level of theory [7, 8].

In order to study and model electronic and molecular structures of M-DNA and the mechanism of its conductivity, we have performed *ab initio* calculations of spatial and electronic structures, thermodynamic properties of adenine-thymine and guanine-cytosine base pairs with Zn^{2+} and Ni^{2+} ions located between the bases as well as the (AC)(TG) stacking dimer of base pairs on nucleic acids with two zinc ions. Particular aims of the present work are to study the adenine-thymine base pair and the dimer including all four bases of nucleic acids (as in DNA) but not only guanine and cytosine bases as in [5, 6]. In this work nickel was used as a transition metal. For these aims we used MP2 level of theory. Studies on the molecular structure of base pairs with the metal ion attached at N1 of purines are of special interest because earlier works [9, 10] investigated mainly the molecular structure of base pairs with the metal ion attached at N7 of purines.

Methods of calculation

In calculations we applied models differing from those investigated in works [5, 6]. In our models metal ions were placed from the side of DNA minor groove. The metal ion was connected with the hydroxyl and with one or two molecules of water. As well, we calculated base pairs with metal ions included but without the hydroxyl and without water molecules as auxiliary models.

Total energies, spatial and electronic structures of adenine-thymine (AT) and guanine-cytosine (GC) pairs and their complexes with Zn^{2+} and Ni^{2+} (ATZn^+ , GCZn^+ , GCNi^+), of the complex of AT pair with Ni^{2+} and hydroxyl (ATNiOH), neutral adenine molecule (A), adenine protonated at N1 (Ap), thymine (T), guanine (G), cytosine (C) were calculated at DFT, MP2 and UMP2 (for Ni^{2+} complexes) levels of theory using 6–31+G* basis set (except GCNi^+ and ATNiOH complexes) by means of Gaussian03 and Gamess (R5) software packages [11, 12]. 6–31G* basis set was used for last Ni^{2+} complexes. AT and GC pairs with Zn^{2+} , hydroxyl and two water molecules ($\text{ATZnOH}(\text{H}_2\text{O})_2$ and $\text{GCZnOH}(\text{H}_2\text{O})_2$ clusters) were also calculated at MP2 levels of theory using 6–31+G* basis set. Hydroxyl (OH^-) in ATNiOH complex, in $\text{ATZnOH}(\text{H}_2\text{O})_2$ and $\text{GCZnOH}(\text{H}_2\text{O})_2$ clusters modeled the alkaline environment. In these clusters water molecules located above and under Zn^{2+} modeled nucleic acid bases are neighbors in a stack in DNA macromolecule. Modeling of a ligand part by water molecules is a usual procedure [13]. MP2 level of theory with 6–31G* basis was used in calculations of (AC)(TG) stacking dimer of base pairs with two zinc ions, two hydroxyls and two water molecules.

As well, calculations of Zn^{2+} or Ni^{2+} with six water molecule assemblies and Zn^{2+} with hydroxyl (ZnOH^+) surrounded by seven water molecules have been carried out.

Full geometry optimizations of complexes and clusters were performed at B3LYP/6–31+G* and MP2/6–31+G* levels of theory, and all the optimized geometries at B3LYP/6–31+G* level were found to be true minimum by respective harmonic vibrational frequencies obtained from diagonalization of force constant matrices with the corresponding Hessian eigenvalues being positive. Interaction energies in complexes have been calculated at MP2/6–31+G* levels of theory by the usual scheme [5, 14]. These energies were computed as energy differences between the optimized complex and optimized components and corrected for the basis set superposition error (BSSE). Calculations of electronic transition energies for complexes AT and GC pairs with Zn^{2+} and Ni^{2+} were performed at TD B3LYP or TD UB3LYP levels of theory at MP2/6–31+G* or UMP2/6–31G* (for Ni^{2+} complexes) reference geometries. Charges on atoms were determined by Mertz-Kolman method [15]. Visualization of the spatial structure and molecular orbitals has been performed by means of Chem-Craft program [16].

Results and discussion

Molecular structure

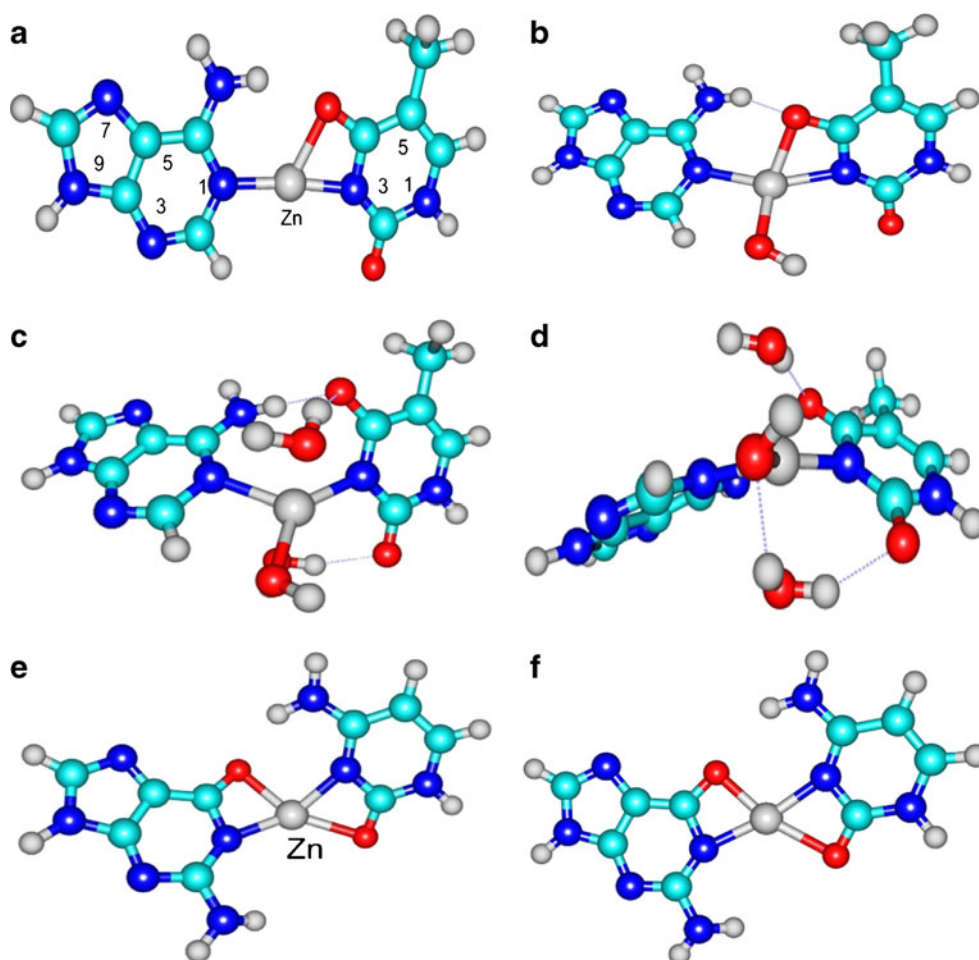
The spatial structure of AT pair complexes with metal ions has not been studied in [5, 6], therefore we begin this discussion of the molecular structure of M-DNA fragments with considering structures including AT pair and metal ions.

As Fig. 1a shows, in the case of the formation of the triple complex of adenine with thymine and Zn^{2+} (ATZn^+) Zn^{2+} forms three coordinating bonds with N1 atom of adenine and N3 and O8 atoms of thymine.

Lengths of these bonds are presented in Table 1. The hydrogen bond between adenine N10 and thymine O8 was kept (the distance between these atoms is only by 0.1 Å more than that between corresponding atoms in AT pair). The structure of the complex is almost planar, and the dihedral angle between planes of the bases being 176.1°.

When forming a complex of adenine with thymine, hydroxyl and Ni^{2+} (ATNiOH), Ni ion forms four coordinating bonds with adenine N1 atom, N3 and O8 atoms of thymine and with hydroxyl oxygen (Fig. 1b, Table 1). A hydrogen bond between adenine N10 and thymine O8 atoms was kept. The structure of the complex is nonplanar, and the dihedral angle between planes of the bases is equal to 168.3°. There is a rather big propeller twist (Table 1) in this complex.

Fig. 1 Structure formulas of calculated complexes and clusters: ATZn + (a), ATNiOH (b), ATZnOH(H₂O)₂ (c, d), GCZn + (e) and GCNi + (f). It is shown that two water molecules are placed above and under Zn ion in ATZnOH(H₂O)₂ cluster



As indicated above, the spatial structure of this complex is nonplanar, in particular, being conditioned with the fact that transition metal ions (as zinc ones too) form readily nonplanar tetrahedral coordination complexes [6, 17]. Particularly,

owing to this fact, the formation of bridges between ions in polyG-polyC macromolecule is possible [6].

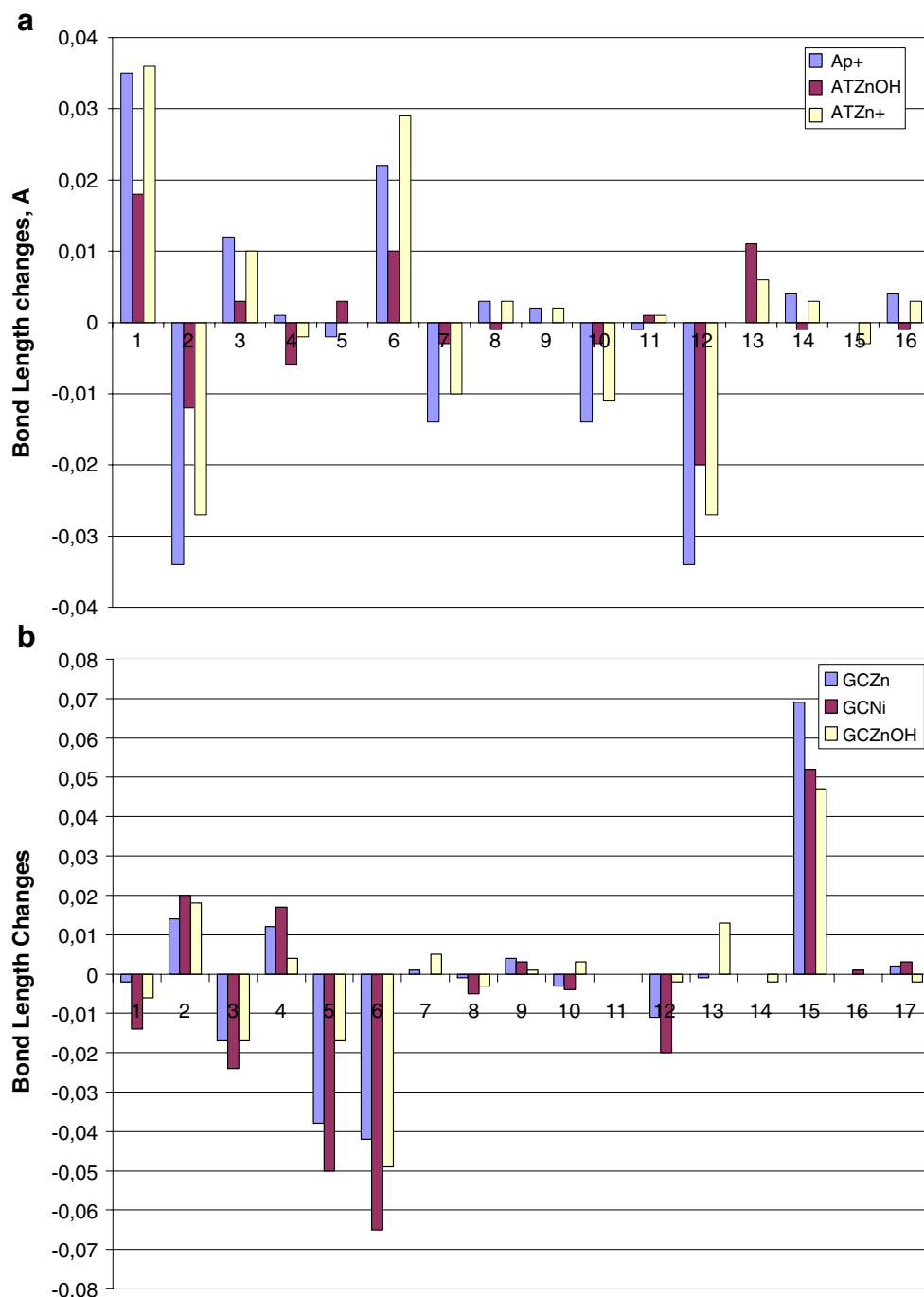
When forming a cluster of AT pair with Zn²⁺, hydroxyl and two water molecules (ATZnOH(H₂O)₂) (Fig. 1c, d),

Table 1 Distances between Zn²⁺ or Ni²⁺ ions and nearest nucleic acid base atoms in calculated complex/clusters (Å⁰) and angles between planes of nucleic acid bases. Designations in Table 1: N1-Me is distance between N1 atom of adenine or guanine and metal ion, O-Me is distance between O10 atom of guanine and metal ion, N3'-Me being distance between N3 atom of thymine or cytosine and

metal ion, O'-Me is distance between O atom of thymine or cytosine and metal ion, OH-Me being distance between O atom of hydroxyl and metal ion, Me-H₂O is distance between O atom of water and metal ion, Dihed - is dihedral angle between base planes (degrees), Propel - being propeller twist between base planes(degrees)

Complex/ Cluster	N1-Me,	O-Me,	N3'-Me,	O'-Me,	OH-Me,	Me-H ₂ O,	Dihed	Propel
ATZn+	1.898		1.897	2.096			176.0	0
ATNiOH	2.071		2.055	2.128	1.827		179.1	23.2
ATZnOH (H ₂ O) ₂	2.124		2.039		1.893	2.241 2.310	148.2	64.3
GCZn ⁺	1.948	2.202	2.007	2.091			157.6	32.3
GCNi ⁺	1.961	2.140	1.982	1.926			172.9	1.4
GCZnOH (H ₂ O) ₂	1.991		2.080		1.894	2.123	138.6	80.3
Zn ²⁺ 6H ₂ O						2.106		
Zn-OH ⁺ 7H ₂ O					1.897	2.055 2.185 2.206 2.090		
Ni ²⁺ 6H ₂ O						2.071		

Fig. 2 Changes in bond lengths (a) for adenine in protonated adenine, in $ATZn^+$ complex and $ATZnOH(H_2O)_2$ cluster, (b) for guanine in $GCZn^+$, $GCNi^+$ complex and $GCZnOH(H_2O)_2$ cluster. Designations of bond lengths at abscissa axes: in Fig. 2a: 1 - N1-C2; 2 - C2-N3; 3 - N3-C4; 4 - C4-C5; 5 - C5-C6; 6 - N1-C6; 7 - C5-N7; 8 - N7-C8; 9 - C8-N9; 10 - C4-N9; 11 - C2-H11; 12 - C6-N10; 13 - N10-H12; 14 - N10-H13; 15 - C8-H14; 16 - N9-H15. in Fig. 2b: 1 - N1-C2; 2 - C2-N3; 3 - N3-C4; 4 - C4-C5; 5 - C5-C6; 6 - N1-C6; 7 - C5-N7; 8 - N7-C8; 9 - C8-N9; 10 - C4-N9; 11 - N1-H (Zn); 12 - C2-N11; 13 - N11-H12; 14 - N11-H13; 15 - C6-O10; 16 - C8-H14; 17 - N9-H15



Zn^{2+} makes three coordinating bonds with N1 of adenine, N3 of thymine and with oxygen of hydroxyl, bond lengths being 2.124 Å, 2.039 Å and 1.893 Å, respectively. Water molecules form hydrogen bonds with thymine O7, oxygen of hydroxyl (the bottom water molecule) and thymine O8 (the top molecule). As a result of the formation of hydrogen bonds with water molecules, the structure of the cluster is essentially nonplanar. The dihedral angle between planes of the bases is equal to 148.2° and the propeller twist of bases makes up 64.3°. Distances from Zn^{2+} to oxygen of the top and bottom water molecules are equal to 2.241 Å and

2.310 Å, respectively, i.e., they are less than the sum of Van-der- Waals radii of the atoms considered.

Changes in bond lengths of N1-Me (in comparison with N1-H11 bond length) are not shown because of their large values ($>0.7\text{Å}$) in Fig. 2b.

Let us analyze changes in the spatial structure of adenine and thymine upon zinc ion incorporation between these nucleic acid bases.

Analysis of bond lengths in $ATZn^+$ complex (Fig. 2a), in $ATZnOH(H_2O)_2$ cluster and protonated adenine, in comparison with bond lengths of the isolated adenine, has

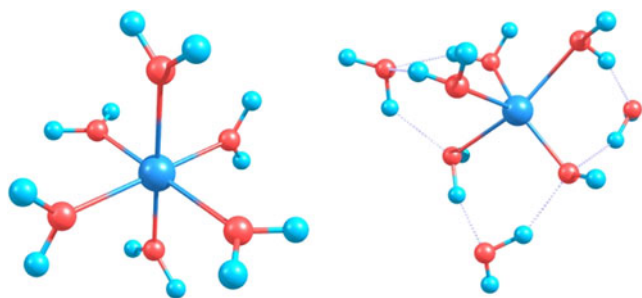


Fig. 3 Calculated molecular structures of Zn^{2+} (left) and $ZnOH^+$ (right) in hydrate shells

shown that upon the formation of complexes with Zn^{2+} more than 0.02 Å change in bond lengths was observed in the adenine molecule on N3-C2-N1-C6-N10 fragment (Fig. 2) that includes N1 atom taking part in the formation of the coordinating bond. Changes in bond lengths of $ATZnOH(H_2O)_2$ cluster are at the module less than those in $ATZn^+$ complex and in protonated adenine. Similar changes in bond lengths in the structures indicated are in agreement with the hypothesis on the analogous effect of protonation and coordination with the metal ion on physical properties of nucleic acid bases [18]. Bond lengths of thymine changed essentially (more than by 0.015 Å) on N3-C4-C5-C6-N1-C2 fragment of the pyrimidine ring and on the exocyclic fragment C4-08 taking part in the formation of coordination and hydrogen bonds.

It is known that calculations on the molecule spatial structure by MP2 method agree well with experimental X-ray data. In our case comparison of bond lengths calculated and results of X-ray analysis revealed good agreement between calculated and experimental bond lengths both for the neutral adenine molecule and the protonated form as well as for the adenine-thymine pair [19, 20]. Differences between calculated and experimental bond lengths are $\pm 1.5\%$.

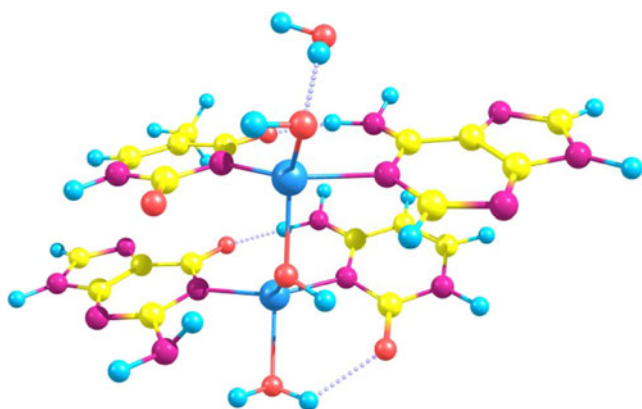


Fig. 4 Optimized molecular structure of (AC)(TG) stacking dimer with two Zn^{2+} , two hydroxyls and two water molecules

Table 2 Angles between and in base pairs of stacking dimer calculated

Angles	(AC)(TG) 2Zn 2OH-2H2O
Helical twist between base pairs, degrees	2
Propeller twist in pair showed, degrees	13 in AT 20 in GC
Dihedral angle in pair showed, degrees	175.4 in AT 174.4 in GC

Structural peculiarities of complexes and of the cluster of metal ions with guanine and cytosine participations are shown in Figs. 1e, f and 2b and in Table 1.

Figure 3 and Table 1 present optimized structures and bond lengths in the calculated complexes of Zn^{2+} and Ni^{2+} with six water molecules and of Zn ion with hydroxyl ($ZnOH^+$) modeling the alkaline environment, with seven water molecules. We did not succeed in calculating zinc complexes with the hydroxyl and five water molecules as the fifth water molecule preferred the formation of two hydrogen bonds with water molecules available.

Table 1 demonstrates distinctions in bond lengths of water molecules forming the coordinating bonds with $ZnOH^+$.

Dimer

As well, at MP2 level of theory, we calculated (AC)(TG) stacking dimer of nucleic acid base pairs with two zinc ions, two hydroxyls and two water molecules. The common form of the dimer (Fig. 4) is similar to those of structures examined in [5, 6] and calculated by DFT method. Base pairs are almost parallel to one another, and bridge bonds take place between base pairs.

As old DFT methods reproduces stacking interactions imperfectly well, let us analyze the molecular structure calculated at MP2 level of theory with 6–31G* basis set.

The peculiarity of the spatial structure of the calculated dimer with zinc ions is bridge bonds between base pairs formed with zinc ions and oxygens of hydroxyls. In particular, the formation of bridges between ions is induced

Table 3 Distances between Zn^{2+} ions and neighbors atoms (Å) in base pairs of stacking dimer calculated

AT-Zn ⁺		GC-Zn ⁺	
Zn-N1 ade	2.145	Zn-N1 gua	1.950
Zn-N3 thy	2.003	Zn-N3 cyt	2.014
Zn-O (OH up)	1.863	Zn O (OH up)	1.920
Zn-O (OH down)	1.983	Zn-O (H2O down)	2.071

with the fact that zinc ions, as transition metal ones, are able to form nonplanar tetrahedral complexes [6, 17]. This was demonstrated above by the example of complexes of base pairs with hydroxyl, zinc ion and two water molecules (Fig. 1c). In the dimer investigated, distance between planes of base pairs are 3.2 Å on average. This distance is smaller than the interfacial distance in DNA B-form but agrees with data from work [21, 22] in which the molecular structure of dimers of nucleic acid base pairs is calculated by MP2 method. Base pairs in dimer with zinc ions are nonplanar. Dihedral angles between bases are of 175° and 174° for AT and GC pairs, respectively. Base pairs in dimer are rather more plane (flat), in comparison with above clusters of base pairs with ions, hydroxyls and water molecules (Table 2). All the pairs in dimers are rather large propeller twists (Table 2) and the distances between the ions and atoms are shown in Table 3.

However our preliminary calculations of (CAC)(GTG) trimer geometry [8] revealed a significant decrease of the dihedral angle and the propeller twist for the middle AT pair in trimer. The dihedral angle in this AT pair and the propeller one are 180° and 0°, respectively. This permits a supposition that base pairs in M-DNA are more plane than those in the dimer calculated.

In dimer, the zinc ion contacting with AT pair forms four bonds, namely: two bonds with adenine N1 and thymine N3 atoms and two bonds with two oxygens of hydroxyls (the own hydroxyl of its pair and of the neighboring one). In dimer the zinc ion contacting with CG pair forms four bonds also- two bonds with guanine N1 and cytosine N3 atoms, one bond with oxygen of the water molecule and one bond with hydroxyl oxygen. One hydrogen bond is kept in base pairs of dimer.

Comparison of bond lengths in base pairs in dimer with zinc ions and in cluster with this ion reveals their substantial similarity. For example, for adenine these distinctions are of

quite small value (~0.1%) (besides N1-C2 and N1-C6 bonds for which changes in bond lengths is about 1%). The helical twist of the dimer considered is of 2° although the initial 40° helical twist was preset.

Thus, upon metal placing between bases in clusters and dimers investigated, the metal ion forms four coordination bonds – two with nitrogen atoms of bases and two with hydroxyl and water oxygens. Because of the ability of transition metal and zinc ions to form tetrahedral coordination spheres in dimer of base pairs, bridges are created between base pairs. All this correlates with results obtained in [6]. Because of bridges formed between base pairs and because of stacking interaction, base pairs in dimer flatten noticeably. Clusters consisting of canonic base pairs, the metal ion, hydroxyl and two water molecules can be a model of the base pair with the metal ion in the dimer content.

Interaction energies

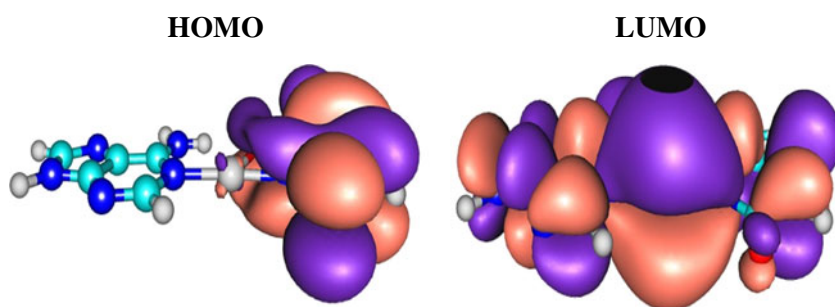
Calculations of interaction energies in AT and GC pairs and in the same pairs with Zn²⁺ and Ni²⁺ as well as in clusters (Table 4) were carried out to elucidate reasons of Zn²⁺ and Ni²⁺ insertion between bases of the pairs studied.

The calculation has shown that the interaction energies are equal to 10.83 kcalmol⁻¹ in AT pair (between adenine and thymine) and 20.14 kcalmol⁻¹ in the guanine-cytosine pair that corresponds to the experimental and calculated data [14, 23, 24]. As well, the calculation has revealed that the interaction energy of Zn²⁺ with adenine and thymine molecules in ATZn⁺ complex is considerably higher than that of imino-proton with adenine and thymine anion and than that of Zn²⁺ with its hydrate environment (six water molecules). Interaction energies are -447.14 kcalmol⁻¹, -363.13 kcalmol⁻¹ and -312.37 kcalmol⁻¹, respectively. As well, the analogous situation occurs for the complex of GCZn⁺ and imonoproton in GC pair

Table 4 Calculated interaction energies (kcalmol⁻¹) in adenine-thymine-zinc (ATZn⁺), guanine-cytosine-zinc (GCZn⁺), guanine-cytosine-nickel (GCNi⁺) complexes, adenine-thymine-zinc-hydroxyl-2H₂O ((ATZnOH(H₂O)₂), guanine-cytosine-zinc-hydroxyl-2H₂O ((GCZnOH(H₂O)₂), clusters, zinc-6H₂O (Zn-6H₂O²⁺), zinc-hydroxyl-7H₂O (ZnOH-7H₂O⁺), nickel-6H₂O complexes and adenine-thymine (AT), guanine-cytosine (GC) pairs

Complex /cluster	Components	Interaction energy, kcal/mol
AT	(A + T)	-10.83
GC	(G + C)	-20.14
AT	(AT ⁺ + H ⁺)	-363.13
GC	(GC + H ⁺)	-358.23
ATZn ⁺	(AT + Zn ²⁺)	-447.14
GCZn	(GC + Zn ²⁺)	-424.40
Zn ²⁺ 6H ₂ O	(Zn ²⁺ + 6H ₂ O)	-312.37
ATZnOH(H ₂ O) ₂	(Zn-OH ⁺ + AT(H ₂ O) ₂)	-265.24
GCZnOH(H ₂ O) ₂	(Zn-OH ⁺ + GC(H ₂ O) ₂)	-273.03
ZnOH ⁺ 7H ₂ O	(Zn-OH ⁺ + 7H ₂ O)	-185.89
GCNi ⁺	(Ni ²⁺ + GC ⁻)	-437.87
Ni ²⁺ 6H ₂ O	(Ni ²⁺ + 6H ₂ O)	-324.29

Fig. 5 HOMO (left) and LUMO (right) orbitals of AT pair and ATZn^+ complex, calculated at MP2 level of theory



Besides, the calculation has shown that the interaction energy of Zn^{2+} and hydroxyl (ZnOH^+) with adenine and thymine molecules in $\text{ATZnOH}(\text{H}_2\text{O})_2$ cluster is considerably higher than that of ZnOH^+ and its hydrate environment ($-265.24 \text{ kcalmol}^{-1}$ and $-185.89 \text{ kcalmol}^{-1}$, respectively). As well, for $\text{GCZnOH}(\text{H}_2\text{O})_2$ cluster the energy of ZnOH^+ + group interaction with guanine and cytosine molecules and two molecules of water is higher than that with its hydrate shell. All this makes the zinc ion position between nucleic acid bases favorable. Calculations of interaction energies in GCNi^+ , $\text{Ni}^{2+}6\text{H}_2\text{O}$ complexes and the analogous interaction energy of iminoproton in GC pair revealed the preference of the nickel ion placing between nucleic acid bases in GCNi^+ complex.

All this makes favorable the insertion of Zn^{2+} and Ni^{2+} between the bases of nucleic acids.

The energy of the vertical interaction between base pairs in dimer with the zinc ion is $37.4 \text{ kcalmol}^{-1}$. It is significantly higher than the energy of the stacking interaction between pairs of canonical bases [21, 22]. However, it should be remembered that in this case the

vertical interaction energy includes energy of the coordination bond between the zinc ion and hydroxyl oxygen being a part of the neighboring pair.

The energy of the horizontal interaction in dimer between the stack (AC) and the rest part of the stacking dimer is $98.60 \text{ kcalmol}^{-1}$ that is significantly higher than the sum of hydrogen bonds in AT and GC pairs (see Table 4) and is the result of changes of hydrogen bonds in base pairs with coordination ones. The rise of horizontal and vertical interactions in the dimer studied permits a supposition that, in comparison with DNA B-form, M-DNA must be more thermal stable. This is in agreement with experimental observation in work [1].

Orbitals

Analysis of forms of high occupied (HOMO) and low occupied (LUMO) molecular orbitals of AT and GC base pairs with zinc and nickel ions is of significant interest. As Fig. 5 shows, only thymine orbitals take part in the formation of HOMO of AT base pair complex with the

Fig. 6 Calculated at UDFT level of theory, HOMO and LUMO of ATNiOH (up) and GCNi^+ (down) complexes

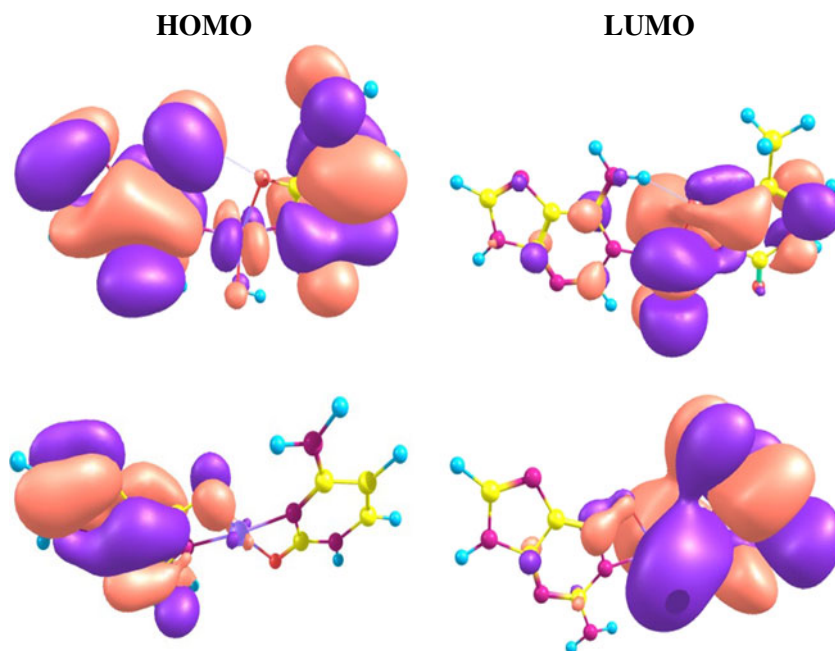
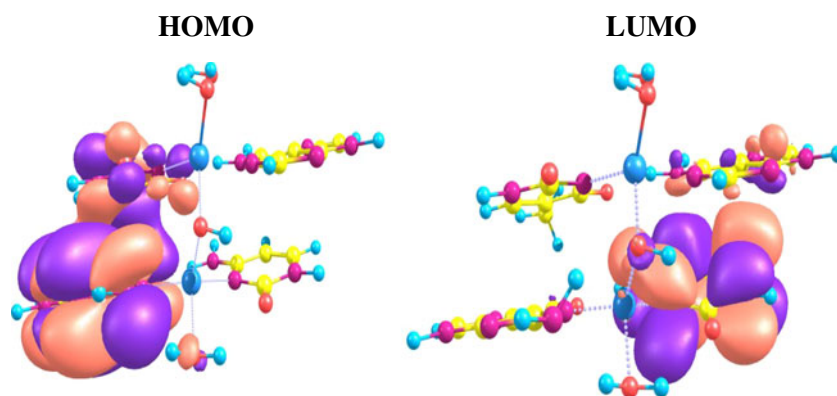


Fig. 7 HOMO (left) and LUMO (right) of (AC)(TG) stacking dimer with two Zn^{2+} , two hydroxyls and two water molecules



zinc ion while orbitals of adenine, zinc ion and thymine participate already in the formation of this complex LOMO. As a result, sizes of the molecule orbital increase essentially, and electron delocalization within two bases in the electron-excited state is possible.

At the same time in complexes of AT and GC pairs with the nickel ion (Fig. 6) orbitals of Ni^{2+} ion take part in HOMO formation as well as in LUMO formation. Our observations of participating nickel ion orbitals in the formation of HOMO complex of GC pair with the nickel ion agree with results of the work [6] in which complexes of GC pair with Co^{2+} and Fe^{2+} ions were calculated and the participation of these ions in HOMO formation was shown. At that, it should be noted that our calculations by B3LYP method also show the participation of orbitals of nucleic acid bases (guanine, adenine and thymine) in the formation of HOMO of complexes studied but not only the participation of metal ion orbitals (as shown in [6]). As well, it should also be noted that nickel ion orbitals take part in the formation of HOMO of the complexes studied only in calculations carried out by UB3LYP method. HOMO determined at UMP2 level of theory do not include orbitals of the nickel ion. Only HOMO-1 calculated at UMP2 level of theory contains nickel ion orbitals.

Analysis of HOMO form of dimer with zinc ions being studied is of significant interest. It is seen from Fig. 7 (left) that this HOMO includes molecular orbitals of neighboring

(in the stack) bases. As well, this figure demonstrates partial overlapping of π -orbitals in top and bottom bases that show possible electron delocalization in the stacking structure calculated. This agrees with a supposition (see work [6]) that electrical conductivity in Zn-DNA is caused with overlapping of π -orbitals of nucleic bases in the stack. At the same time Fig. 7 (left) shows the absence of contribution of zinc ion orbitals into HOMO dimer. LUMO of dimer includes mainly cytosine orbitals (Fig. 7 (right)).

The preliminary calculation of (AC)(TG) stacking dimer with two Ni^{2+} , two hydroxyls and two water molecules showed that adenine orbitals mainly take part in HOMO of this structure. There are small contributions of Ni^{2+} orbitals in HOMO and HOMO-1

Charges on metal ions

Consider changes of charges on zinc and nickel ions upon their formation of complexes and clusters and during the ion entering into dimer. As Table 5 shows, charges on metal ions decrease significantly (from +2 to +1) in all the systems studied. The decrease is caused by the transfer of the electron density from nucleic acid bases to vacant orbitals of the ion.

Electronic transition energies

Studying electronic transition energies in complexes of AT and GC pairs with Zn and Ni ions is of great interest. The calculation of singlet electronic transition energies has shown that, in comparison with corresponding energies of AT and GC pairs, there is only a small reduction (0.3–0.6 eV) of the energy of the first singlet excited state for complexes AT and GC pairs with Zn^{2+} .

At the same time energies of the first singlet excited states (Table 6) essentially decrease (from 4.5 eV to 0.4–0.6 eV) in complexes of GC and AT pairs with Ni^{2+} ion. It specifies an opportunity of the significant narrowing

Table 5 Calculated charges of Zn^{++} or Ni^{++} in complexes with Thymine, Guanine and AT and GC pairs, in clusters and in dimer

Ion/structure	TZn+	ATMe	ATMeOH (H ₂ O) ₂	Dimer
Zn ⁺⁺ , MK	1.458	1.280	0.918	1.033
Ni ⁺⁺ , Mullik		1.295	0.686	
	GZn+	GCMc	GCMcOH(H ₂ O) ₂	Dimer
Zn ⁺⁺ , MK	1.411	1.263	0.954	1.058

Table 6 Parameters of GCNi⁺ (left), ATNiOH (right) excited states calculated on geometries by TD DFT method on UMP2 level of theory

Excited state	Excited state energies, eV GCNi ⁺	Wave length, nm	Oscil. streng.	Excited state energies, eV ATNiOH	Wave length, nm	Oscil. streng.
1	0.391	3911	0.0001	0.586	2117	0.0001
2	0.821	1510	0.0000	0.718	1725	0.0002
3	1.341	924	0.0033	0.999	1220	0.0001
4	2.126	583	0.0001	1.806	689	0.0003
5	2.157	574	0.0007	2.096	591	0.0002
6	2.431	510	0.0016	2.392	518	0.0008
7	2.506	495	0.0046	3.368	379	0.0001
8	2.703	459	0.0005	3.505	354	0.0011
9	2.714	457	0.0001	3.546	349	0.0119
10	2.865	432	0.0327	3.790	327	0.0027

of the band gap in DNA and polynucleotides containing the introduced Ni ions. These results agree with the narrowing of the band gap in GC polynucleotide with Fe²⁺ and Co²⁺ ions, considered in work [6]. Our results calculated also explain (see 6, 7 lines in Table 6) the weak light absorption of Ni²⁺ form on M-DNA in the range of 500 nm, referred in work [1].

Conclusions

Molecular and electronic structures of complexes and clusters including canonical pairs of AT and GC bases with zinc and nickel ions located between bases are calculated at MP2 level of theory. As well, the (AC)(TG) stacking dimer of base pairs of nucleic acids with zinc ions is estimated.

Changes in adenine and guanine spatial structures upon zinc and nickel ions attaching to purine N1 were analyzed.

It was shown that the energies of zinc and nickel ion interactions in complexes with nucleic acid bases studied is essentially higher than that of imino proton cooperation with canonical bases in AT and GC pairs. The energy of zinc and nickel ion interactions with nucleic acid bases is higher than that of these ion interactions with their hydrate shells.

HOMO of stacking dimer with zinc ions investigated includes molecular orbitals of neighboring (in the stack) bases.

Charges on metal ions incorporated into complexes with nucleic bases and in dimer decrease significantly.

The calculation of electronic transition energies has shown the decrease of the first singlet transition energies in complexes of AT and GC pairs with Ni ion from 4.5 eV to 0.4–0.6 eV.

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