

DFT Calculations of Space Structures of M^{II} Complexes with (N,N,N,N) -Coordinating Macroheterocyclic Ligand – 1,8-Dioxa-3,6,10,13-tetraazacyclotetradecanetetraethione-4,5,11,12

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Geometric parameters of Mn^{II} , Co^{II} , Ni^{II} and Cu^{II} complexes with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetraethione-4,5,11,12 - macroheterocyclic ligand with N,N,N,N -coordination mode, which can be formed as a result of template processes in M^{II} – ethanedithioamide-1,2 – methanal triple systems, were calculated using DFT B3LYP method with 6-31G(d) basic set. Additional 6-membered metal chelate cycles formed as a result of template “stitching” are not planar and considerably tilted in respect to two 5-membered cycles. In addition, in V^{IV} complex, both these cycles are on one side from the mean N,N,N,N -plane formed by coordinating nitrogen atoms, in all other complexes – on different sides of this plane.

Keywords: Macrocylic complexes, template synthesis, space structure, DFT B3LYP method.

Introduction

It was found earlier that a template synthesis in the M^{II} ion – ethanedithioamide-1,2 [$H_2N-C(=S)-C(=S)-NH_2$] – methanal [CH_2O] triple systems proceeds into metal hexacyanoferrate(II) - gelatin-immobilized matrix implants (MHF-GIM, $M=Co, Ni, Cu$), and, also, some details concerning of coordination of ligand formed as a result of such synthesis (what is known as chelant), to corresponding metal ion have been established.^[1-3] According to mass-spectroscopic data, among the other products of such synthesis, the small amounts of (5.6.5.6) macrocyclic complexes **I** with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetraethione-4,5,11,12 are also present. Such macrocyclic complexes are formed in the corresponding GIM according to the reaction (1).

Up to now the space structure of macrocyclic complexes **I** remains the open question because all attempts to obtain their crystals suitable for X-ray diffraction analysis from gelatin matrix, didn't lead to any positive result. Therefore it is interesting to carry out the calculations of metal complexes formed in the given systems using any of

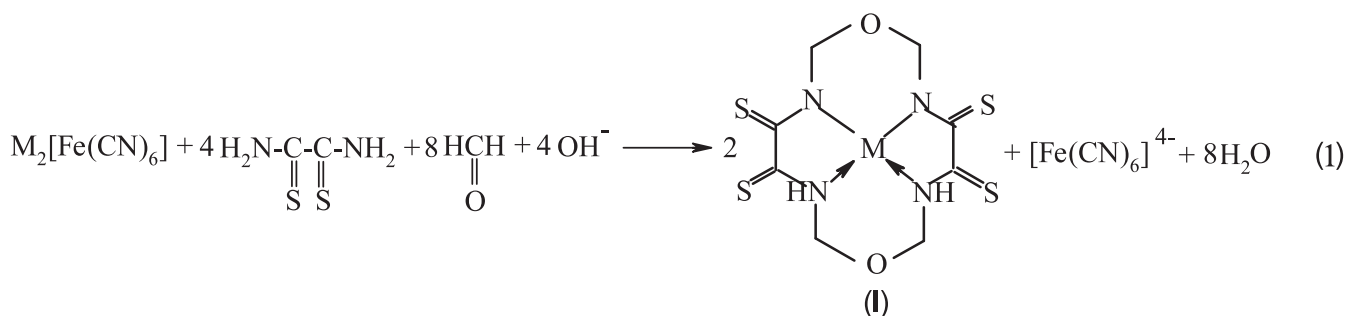
the modern quantum-chemical methods allowing obtaining independent objective data on geometric parameters. In this paper we present and discuss the results of such calculations performed using three-parametric hybrid method of density functional theory – B3LYP.

Method

In our calculations we have employed the B3LYP 6-31G(d) method, which is hybrid DFT method using Becke function (1988) including Slater exchange, by beginning with amendment including density gradient, and correlation function of Lee, Yang and Parr, which includes local and non-local terms.^[4] The energy values E were calculated according to the equation

$$E = V + \langle hP \rangle + 1/2 \langle PJ(P) \rangle + EX[P] + EC[P],$$

where V is nuclear energy of repulsion, $\langle hP \rangle$ – one-electronic (kinetic + potential) energy, $1/2 \langle PJ(P) \rangle$ – energy of electrons repulsion, $EX[P]$ – exchange function; $EC[P]$ – correlation function. 6-31G(d) basic set where each inner atom orbital (AO) is described by six functions of Gauss type (GTO), valence 2s AO- by three GTO, valence p-AO - by one GTO, with addition



of polarization d -GTO to each p -function, was used. Conformity of the found stationary points to energy minima in all cases was proved by calculation of the second derivatives of energy on coordinates of atoms. Every of equilibrium structures corresponding to the minimum points on surfaces of potential energy, had only material values of frequencies. In calculations no limitation in symmetry of complexes was imposed. All calculations were made with using Gaussian98 program.^[5] Time of quantum-chemical calculations of complexes studied was 8-9 months.

Results and Discussion

Numbering of atoms in the studied template complexes is shown in Figure 1; their space structures obtained as a result of quantum-chemical calculations, are presented in the Figures 2-4.

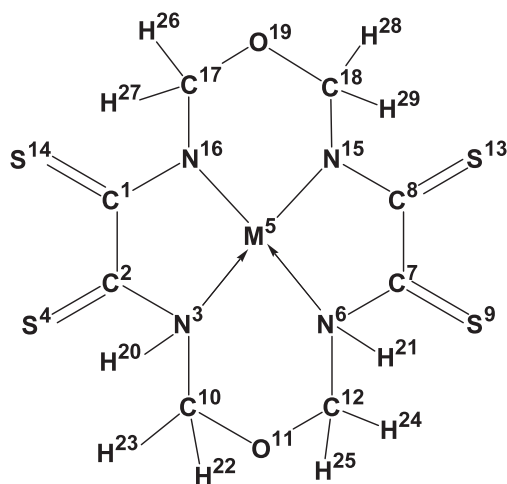


Figure 1. Atoms numbering in the structures of template complexes having general formula **I**.

The macrocyclic complexes **I** of Mn^{II} and Fe^{II} are high-spin, whereas similar Co^{II} and Ni^{II} compounds are low-spin complexes (spin multiplicity of basic state is 6, 5, 2 and 1, respectively). The basic state of V^{IV} , Cu^{II} and Zn^{II} is spin

doublet (V , Cu) and spin singlet (Zn). It should be noted that, in the case of Co^{II} the distinction between energy of basic state (spin doublet) and energy of nearest excited state (spin quartet) is only 7.8 kJ, and, that is why, it may be expected existence of spin-isomeric coordination compounds.

In conformity with theoretical expectations, the grouping of four nitrogen atoms forming chelate unit MN_4 , is ideally plane practically in all compounds of type **I** under examination (sum of angles $\angle N(3)N(6)N(15)$, $\angle N(6)N(15)N(16)$, $\angle N(15)N(16)N(3)$ and $\angle N(16)N(3)N(6)$ is precisely 360.00°). There is only one exception, namely Co^{II} complex where this sum is a little lesser (359.6°). However, MN_4 chelate unit is not plane itself – in all cases M atom is deflected slightly from above-mentioned plane [sum of angles $\angle N(3)M(5)N(6)$, $\angle N(6)M(5)N(15)$, $\angle N(15)M(5)N(16)$ and $\angle N(16)M(5)N(3)$ (VAS) is in the case of V^{IV} 332.3° , Mn^{II} – 336.5° , Fe^{II} – 346.7° , Co^{II} – 356.8° , Ni^{II} – 358.0° , Cu^{II} – 354.5° , Zn^{II} – 347.4°]. It should be noted that, in the each of complexes considered, there are two pairs of equal $M-N$ bond lengths. The same situation is observed for the distances between neighbouring nitrogen atoms in chelate units and for $\angle NMN$ valence angles (Table 1).

This circumstance is evidence that both additional six-membered cycles containing $N-C-O-C-N$ chain formed as a result of template “stitching”, are not in one plane with N_2S_2 donor centers; they are considerably inclined to the flatness even in the case of Co^{II} , Ni^{II} and Cu^{II} complexes having quasi-planar structure. Moreover, the degree of this slope for each of these cycles in the same complex is different as can be readily seen from Figures 2-4. For example, torsion angles $\angle C(12)N(6)N(15)N(3)$ and $\angle C(10)N(3)N(16)N(15)$ which characterise the degree of tilting of the first six-membered cycle and torsion angles $\angle C(17)N(16)N(6)N(15)$ and $\angle C(18)N(15)N(3)N(16)$ reflecting tilting of the second six-membered cycle, in the case of Co^{II} are 80.3° , 76.9° , 10.3° and 1.0° , respectively, and in the case of Ni^{II} , 82.3° , 82.3° , 4.4° and 4.4° , respectively. Moreover these additional six-membered cycles are extremely distorted – in each of them there are no set even

Table 1. $M-N$ and $N-N$ bonds lengths and $\angle NMN$ valence angles in macrocyclic complexes of type **I**.

M	V	Mn	Fe	Co	Ni	Cu	Zn
M–N bond lengths, pm							
M(5)N(3)	217	233	221	197	193	205	222
M(5)N(6)	217	233	221	197	193	205	222
M(5)N(15)	199	202	197	186	185	191	193
M(5)N(16)	199	202	197	187	185	191	193
$\angle NMN$ valence angles, degree							
$\angle N(3)M(5)N(6)$	85.8	85.5	88.2	91.8	91.7	90.9	86.2
$\angle N(6)M(5)N(15)$	76.5	76.6	79.3	84.2	84.6	82.8	79.8
$\angle N(15)M(5)N(16)$	93.6	97.8	99.9	97.1	97.1	98.0	101.6
$\angle N(16)M(5)N(3)$	76.5	76.6	79.3	83.7	84.6	82.8	79.8
N–N bond lengths, pm							
N(3)N(6)	294	317	308	283	277	293	304
N(6)N(15)	258	271	267	257	255	262	267
N(15)N(16)	290	305	301	280	278	288	299
N(16)N(3)	258	271	267	257	255	262	267

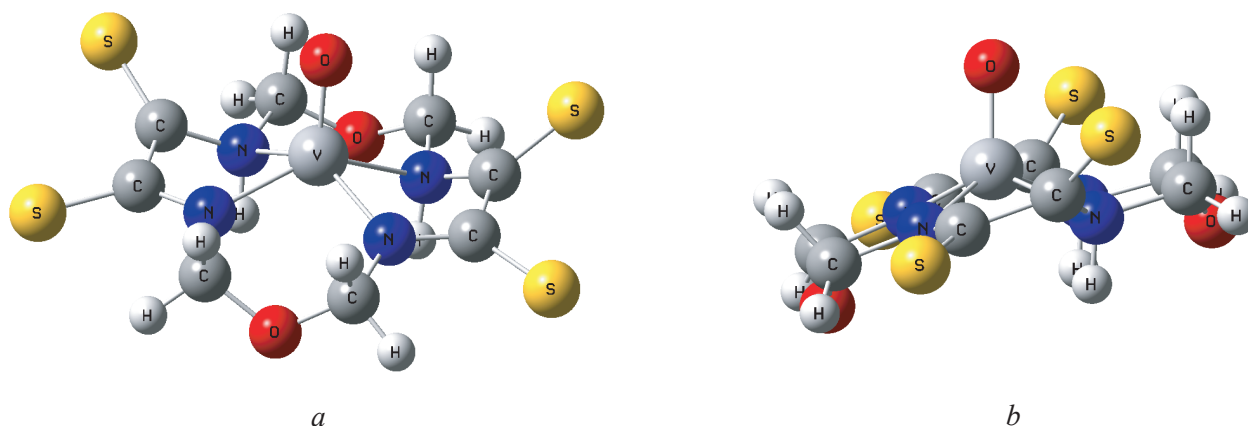


Figure 2. The space structure of V^{IV} complex of type I: “open”, front view (a) and “shielded”, side view (b).

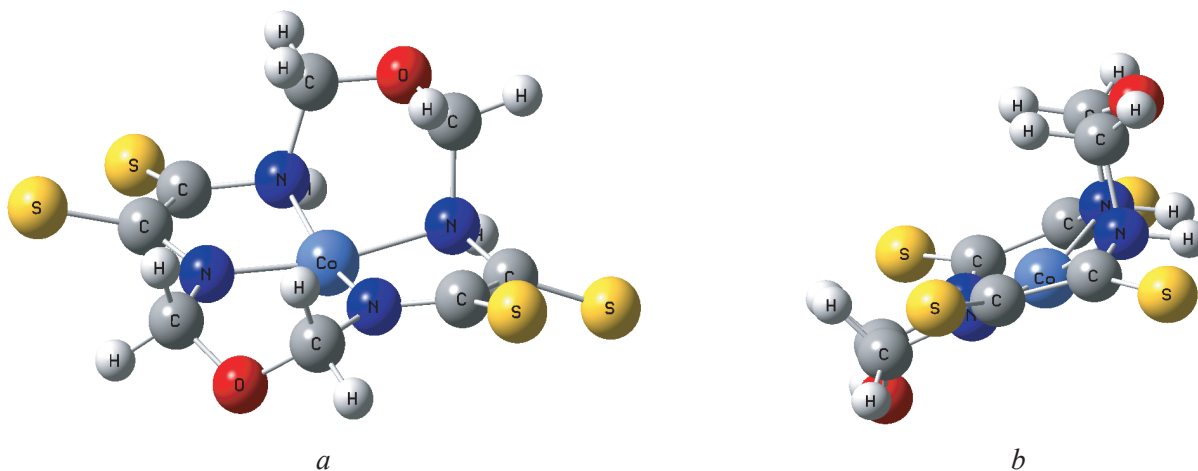


Figure 3. The space structure of Co^{II} complex of type I: “open”, front view (a), and “shielded”, side view (b).

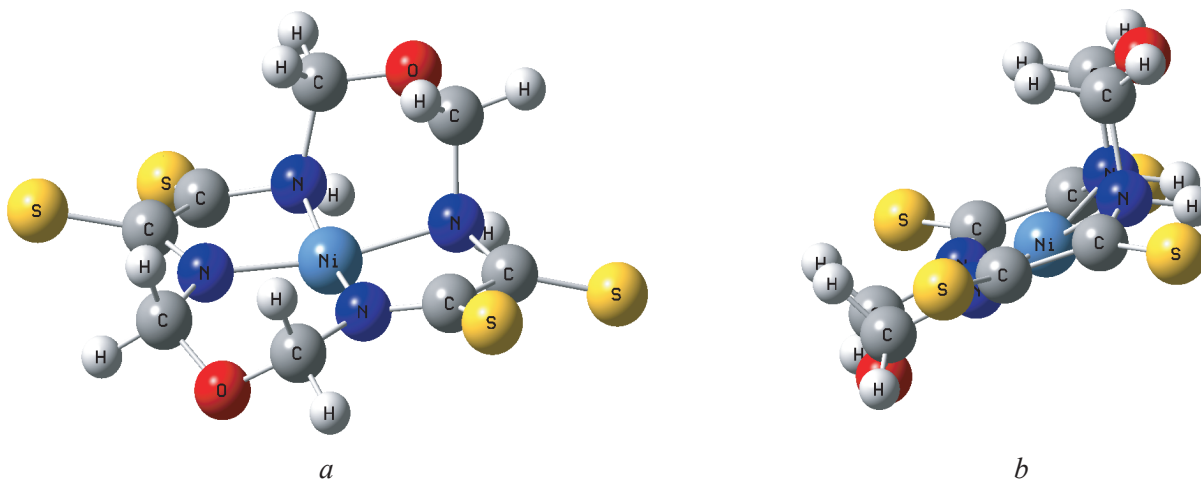


Figure 4. The space structure of Ni^{II} complex of type I: “open”, front view (a), and “shielded”, side view (b).

of four atoms arranged in the same plane. Oxygen atom is considerably displaced from the $N-CH_2-CH_2-N$ plane [torsion angles $\angle O(11)C(12)N(3)C(10)$ and $\angle O(19)C(18)N(15)C(17)$ that may be considered as a degree of this deflection, are, for example, 43.9° and 32.1° in the case of Mn, 36.8° and 31.5° in the case of Ni and 41.6° and 31.5° in the case of Zn). It should be noted in this connection that in V^{IV} complex, both cycles are on the one side of the (NNNN) plane formed by coordinating nitrogen atoms (Figure 2),

whereas in all other complexes – on different sides of this plane (Figures 3,4). Noteworthy, in vanadium(IV) complex oxygen atom connected with vanadium atom is orientated on the one side from the (NNNN) plane, whereas oxygen atoms of the 6-membered chelate cycles, are on the other side (Figure 2). It is interesting that unlike oxygen atoms, sulfur atoms in all studied complexes are on the different sides of (NNNN) plane: two are on one side, and the other two - on the other side (Figures 2-4).

Table 2. Standard thermodynamical parameters of M^{II} complexes with 1,8-dioxo-3,6,10,13-tetraazacyclo-tetradecanetetraethione-4,5,11,12.

M	Standard thermodynamical parameters of formation			Standard thermodynamical parameters of atomization		
	$\Delta H_{f,298}^0$, kJ/mol	$S_{f,298}^0$, J/mol·K	$\Delta G_{f,298}^0$, kJ/mol	ΔH_{298}^{at} , kJ/mol	S_{298}^{at} , J/mol·K	ΔG_{298}^{at} , kJ/mol
V	-20.0	747.2	-12.5	12199.5	3611.7	11122.7
Mn	320.5	734.5	303.8	11375.0	3454.5	10345.0
Fe	395.6	734.7	377.4	11435.9	3461.1	10404.0
Co	340.0	708.0	330.6	11499.6	3486.9	10460.0
Ni	326.4	704.6	317.9	11518.2	3493.0	10476.7
Cu	232.4	711.1	223.0	11520.9	3470.7	10486.1
Zn	248.1	718.7	239.0	11297.6	3457.8	10266.6

The data of the quantum-chemical calculations of values of standard thermodynamic parameters of macrocyclic complexes (**I**) under examination are presented in the Table 2. As may be seen, $\Delta G_{f,298}^0$ values for almost each of these complexes are positive and have extremely high values, which indicates their comparatively small stability. It is interesting that the sole exception is V^{IV} complex for which $\Delta H_{f,298}^0 < 0$ and $\Delta G_{f,298}^0 < 0$.

According to calculations, all complexes with 1,8-dioxo-3,6,10,13-tetraazacyclo-tetradecanetetraethione-4,5,11,12 under examination have extremely large electric dipole moments – 6.13 [V^{IV}], 5.53 [Mn^{II}], 5.73 [Fe^{II}], 6.44 [Co^{II}], 6.52 [Ni^{II}], 6.31 [Cu^{II}] and 5.57 [Zn^{II}] Debye units. As may be seen from these values, the electric dipole moment decreases from V to Mn, increases from Mn to Ni, and decreases again from Ni to Zn. So the considerable values of this parameter are perfectly understandable because, as it may be seen from the Figures 2-4, all they are sharply asymmetric. Besides, electric dipole moment reaches its maximal value for Co^{II} complex, for which, judging by values of valence angles and bonds lengths (Table 1), this asymmetry is the most pronounced.

Conclusions

All macroheterocyclic M^{II} complexes with 1,8-dioxo-3,6,10,13-tetraazacyclo-tetradecanetetraethione-4,5,11,12 considered in the paper, in spite of relatively small amount of cyclic fragments in them (only 4), are not plane; their configuration is either «bowl» on thin «pedestal» [in the case of V^{IV}] or «arm-chair» (in the case of all other 3d-elements considered here). Nevertheless, in all studied complexes four coordinating donor nitrogen atoms are located practically in one plane and the M atoms are only slightly deflected from this (NNNN) plane. At the same time, the character of changing of M–N bonds lengths in V – Zn row, in whole, coincides with character of changing of radiuses of two-charged ions in same row; similar situation

occurs in the case of N–N bonds lengths, too, and, that is very interesting, in the case of degree of deflection of M atoms from (NNNN) plane [which may be quantitatively characterised by the value (360–VAS)^o]. Incidentally, the minimal values of parameters indicated are reached in the case of Ni^{II} complex, the maximal ones – in the case of Mn^{II}. All these complexes are strongly asymmetric and, at the best, have only one element of symmetry, namely symmetry plane passing through M atom and two O atoms contained in 6-membered metal chelate cycles.

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