DFT B3LYP Calculation of Molecular Structures of (5.6.5.6) Macrotetracyclic Fe^{III} and Co^{III} Complexes with 14–Membered Tetraazacyclic Ligand

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Using DFT B3LYP method with 6-31G(d) basic set and Gaussian 98 program, a calculation of geometric parameters of molecular structure of heteroligand Fe^{III} and Co^{III} complexes with macrocyclic ligand (1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetrathione-4,5,11,12) and with N,N,N,N-coordination of donor centres formed as a result of self-assembly processes in the M^{III}– ethanedithioamide-1,2-methanal triple systems, has been carried out. The bond lengths and angles between various atoms in the each of above-mentioned complexes are presented.

Keywords: Macrocyclic complex, template synthesis, molecular structure, DFT B3LYP method.

Introduction

Recently it was found a fact of template synthesis in the M^{III} ion – ethanedithioamide-1,2 [H_2N–C(=S)–C(=S)–NH_2] – methanal CH_2O triple systems proceeding into iron(III) and cobalt(III) hexacyanoferrate(II) gelatin-immobilized matrix implants (GIM),[1,2] and, also, some details concerning of coordination of macrocyclic ligand (what is known as chelant) formed as a result of such synthesis, to corresponding metal ion have been established. According to the mass-spectrometry data, among the other products of the synthesis, *i.e.* (5.6.5.6)macrotetracyclic metal-complexes (**I**) with 14-membered tetraazacyclic ligand, 1,8-dioxa-3,6,10,13-tetraazacyclotetra-decanetetrathione-4,5,11,12, are present at a small amount; such metalmacrocyclic compounds are formed in the corresponding GIM according to probable reaction which may be ascribed by general equation (1).

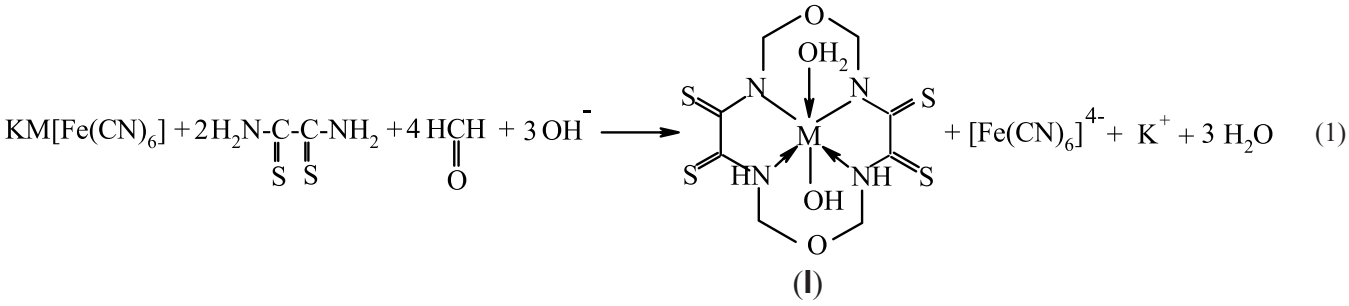
The space structure of macrotetracyclic compounds (**I**) is open question up to now because all attempts to isolate from gelatin matrix their crystals suitable for X-ray diffraction analysis, have not led to any positive result. For this simple reason, it is represented expedient to carry out the calculations of the geometrical parameters of the molecular structure of Fe^{III} and Co^{III} complexes, formed in the given systems, with using any of the modern quantum-chemical methods allowing to obtain independent objective data on the parameters indicated. In this connection, the present paper is devoted to enumeration and discussion of calculation results using one of the such modern quantum-chemical methods, namely three-parametric hybrid method of density functional theory B3LYP. As far as we know, there are no data concerning molecular structure of the (5.6.5.6)macrotetracyclic coordination compounds of type (**I**) in literature and any attempts of quantum-chemical calculations of complexes with using DFT B3LYP method were undertaken till now.

Method

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 therms,[3,4] was used for calculations. The energy values E were calculated according to the equation

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

Here V is nuclearic 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)



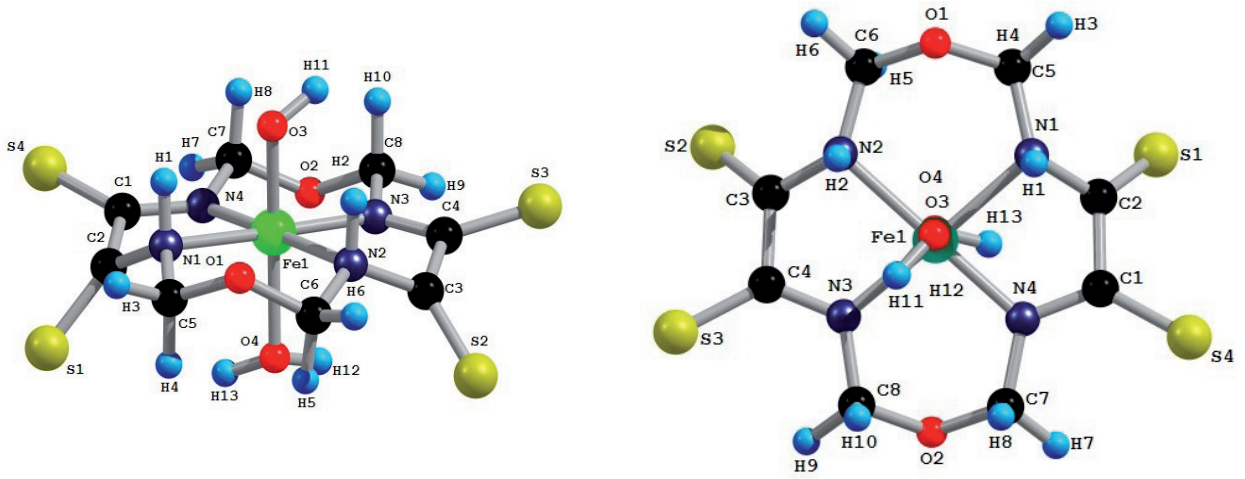
is described by six functions of Gauss type (GTO), valence 2*s* AO - by three GTO, valence *p*-AO – by one GTO, with addition of polarization *d*-GTO to each *p*-function, was used. Confirmity of the found stationary points to energy minima in all cases was proved by calculation of the second derivatives of energy on coordinates of atoms. Every of equilibrium structures corresponding to points of a minimum on surfaces of potential energy, had only material values of frequencies. Any limitation in symmetry of complexes calculated is not imposed. All quantum-chemical calculations were made with using Gaussian98 program[5]and have been carried out with using supercomputer MVS-100000K (10 TFLOPS). Supercomputer MVS-100000K consists of 64 units (blocks) connected Gigabit Ethernet and Infiniband. Each unit consists of two four-nuclear Xeon E5450 processors with cycle frequency 3 GHz and has volume of operative memory 8 Gb.

Results and Discussion

The molecular structures of heteroligand Fe^{III} and Co^{III} complexes with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetrathione-4,5,11,12, H_2O and OH^- ion obtained as a result of quantum-chemical calculations, are presented in the Figures 1 and 2.

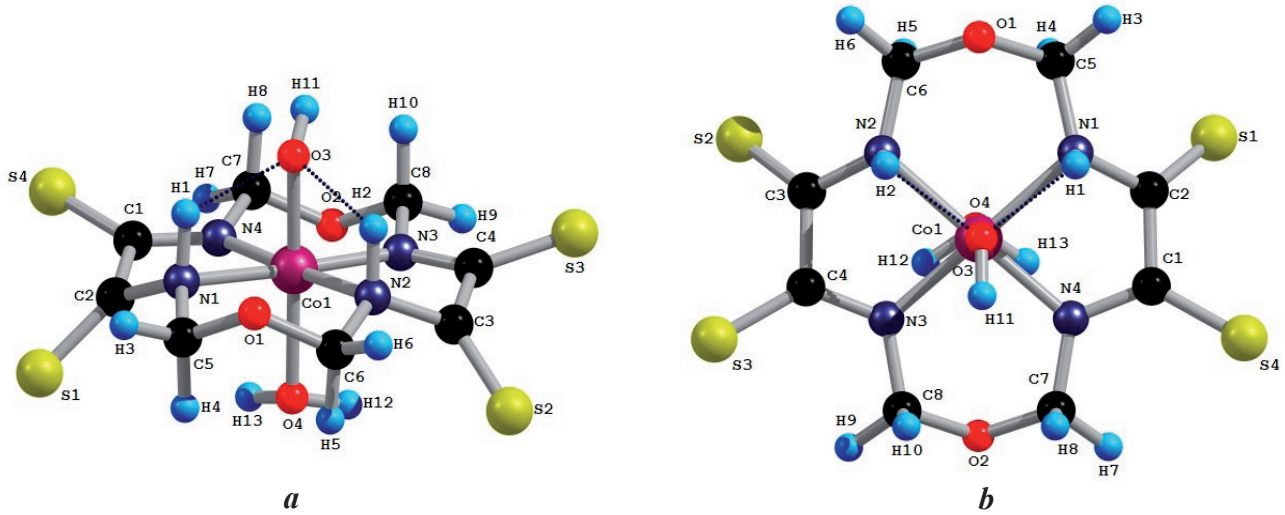
In confirmity to theoretical expectations, the grouping of four nitrogen atoms forming chelate unit MN_4, is ideally plane practically in the both compounds of type (**I**) under examination [sum of angles ∠(N1)(N2)(N3), ∠(N2)(N3)(N4), ∠(N3)(N4)(N1) and ∠(N4)(N1)(N2) is 359.9° (Fe) and 360.0° (Co)]. MN_4 chelate unit may be considered as plane because the sum of angles ∠(N1)(M)(N2), ∠(N2)(M)(N3), ∠(N3)(M)(N4 and ∠(N4)(M)(N1) (VAS) in the case of Fe^{III} complex is 360.0°, in the case of Co^{III} complex is 359.8°. It should be noted that, in the both complexes considered, two of four M–N bond lengths in pairs are equal; similar situation takes place for distances between neighboring nitrogen atoms in chelate units and for ∠NMN valence angles (Table 1).

This circumstance attracts an attention that in the both complexes under examination, the additional six-membered cycles containing N–C–O–C–N grouping formed as a result of template "stitching", is not in one plane with (NNNN) donor centers; it has been rather considerably inclined to flatness indicated. Moreover, the degree of this slope for each of these cycles in the same complex is different. For example, torsion angles ∠(C7)(N4)(N1)(N3) and ∠(C8)(N3)(N2)(N4), which may be considered as a degree of the slope of the first six-membered cycle, and torsion angles ∠(C6)(N2)(N4)(N1) and ∠(C5)(N1)(N3)(N2) which may



a ***b***

Figure 1. The space structure of Fe^{III} complex of type (**I**): the front view (***a***) and the top view (***b***).



a ***b***

Figure 2. The space structure of Co^{III} complex of type (**I**): the front view (***a***) and the top view (***b***). The intra-molecular hydrogen bonds are shown by dotted line.

be considered as a degree of the slope of the second six-membered cycle, in the case of the Fe^{III} complex are 65.4°, 61.2°, 23.4° and 18.3°, and in the case of the Co^{III} complex - 63.5°, 63.5°, 21.6° and 21.6°, respectively. In addition, the each of these additional six-membered cycles is extremely distorted – there are no set even of four atoms arranged in the same flatness, in each of them. At the same time, any of these additional six-membered cycles is not plane.

On the one hand, the sums of angles [∠(M1)(N2)(C6), ∠(N2)(C6)(O1), ∠(C6)(O1)(C5), ∠(O1)(C5)(N1), ∠(C5)(N1)(M1), ∠(N1)(M1)(N2)] and [∠(M1)(N3)(C8), ∠(N3)(C8)(O2), ∠(C8)(O2)(C7), ∠(O2)(C7)(N4), ∠(C7)(N4)(M1), ∠(N4)(M1)(N3)] which may be considered as a degree of deflection of corresponding six-numbered cycle from flatness, in the case of Fe^{III} complex are 665.6° and 674.7°, in the case of Fe^{III} complex are 666.5° and 675.2°, respectively. The values of both sums indicated are considerably lesser than the sum of the internal angles in plane hexagon (720°). On the other hand, oxygen atoms are deflected from $N–CH_2–CH_2–N$ grouping on the rather considerable angle [torsion angles ∠(O2)(C7)(N3)(C8) and ∠(O1)(C5)(N1)(C6), which may be considered as a degree of this deflection, are 39.1° and 32.2° in the case of Fe^{III} complex, and 39.3° and 32.1° in the case of the Co^{III} complex]. It should be noted in this connection that in both complexes these cycles are on different sides of this grouping. It is interesting that sulfur atoms in the both complexes are on different sides of (NNNN) grouping: two - on the one side, the other two - on the other side (Figures 1, 2). In addition, the (CS) bond lengths for S atoms orientated on the same side of (NNNN) grouping [namely (C1)(S4) and (C4)(S3), (C2)(S1) and (C3)(S2)], are practically equal to each other (Table 1).

Three extremely essential distinctions between Fe^{III} and Co^{III} complexes with macrocyclic ligand considered attract an attention. Firstly, according to the data of given calculation, there are two *intra-molecular hydrogen bonds* between oxygen atom of hydroxo group (O3) and hydrogen atoms of iminogroups (H1) and (H2) in the cobalt(III) complex, whereas in the iron(III) complex such bonds are absent. Besides, inter-atomic distances (O3)(H1) and (O3)(H2) in the Co^{III} complex are practically equal (193.7 and 193.8 pm, respectively), while in the Fe^{III} complex they are appreciably distinguished (206.3 and 212.0 pm, respectively). Secondly, in the iron(III) complex lines of bonds (O3)(H11) and (O4)(H12) are practically in one plane (Figure 1*b*), whereas in the cobalt(III) complex, they are in different planes (Figure 2*b*). Incidentally, in the Co^{III} complex, (O4)(O3)(H11) plane divides the angle ∠(H12)(O4)(H13) practically in half. And, finally, thirdly, valence angles ∠(M1)(O4)(H12) and ∠(M1)(O4)(H13) in the Co^{III} complex are equal (104.1°), while in the Fe^{III} complex they are appreciably distinguished among themselves (104.8° and 111.8° respectively).

It is noteworthy that both metalmacrotetracyclic compounds (**I**) considered are low-spin complexes; the basic state in the case of Fe^{III} complex is spin doublet, and of Co^{III} complex - spin singlet. It should be noted especially in this connection that, in the case of Fe^{III}, according to the data of our calculation, distinction between energy of basic state and energy of nearest excited state (spin quartet) is only 6.50 kJ, and, that is why, in principle, one may expect an existence of spin-isomeric coordination compounds. In the

Table 1. Some parameters of molecular structure of heteroligand Fe^{III} and Co^{III} complexes with 1,8-dioxa-3,6,10,13-tetraazatetradecanetetrathione-4,5,11,12; L - H_2O and OH^- ions.

	Fe^{III} complex	Co^{III} complex
Selected bonds	Selected bond lengths, pm	
(M1)(N1)	206.50	201.70
(M1)(N2)	206.21	201.71
(M1)(N3)	191.92	189.63
(M1)(N4)	188.90	189.63
(M1)(O3)	181.33	184.82
(M1)(O4)	205.91	202.49
(C4)(N3)	134.11	134.13
(C2)(N1)	142.91	143.42
(C1)(S4)	166.83	167.14
(C2)(S1)	163.67	163.15
(C3)(S2)	163.13	163.15
(C4)(S3)	167.45	167.14
(N1)(C5)	148.58	148.28
(N2)(C6)	148.25	148.27
(N3)(C8)	145.45	145.37
(N4)(C7)	145.54	145.38
(O1)(C5)	140.66	140.55
(O1)(C6)	140.93	140.55
(O2)(C7)	141.25	141.06
(O2)(C8)	141.39	141.06
Selected valence angles	Selected valence angles, grad	
(N1)(M1)(N2)	96.45	95.50
(N2)(M1)(N3)	81.94	83.36
(N3)(M1)(N4)	98.23	97.61
(N4)(M1)(N1)	83.43	83.37
Sum of valence angles at M atom	360.05	359.84
(M1)(N1)(C2)	102.43	105.70
(M1)(N4)(C1)	116.73	116.81
(M1)(O3)(H11)	113.07	112.25
(M1)(O4)(H12)	104.76	104.09
(M1)(O4)(H13)	111.84	104.12
(N1)(C2)(C1)	110.15	109.68
(M1)(N1)(C5)	116.38	117.54
(M1)(N2)(C6)	115.86	117.53
(M1)(N3)(C8)	119.94	120.56
(M1)(N4)(C7)	119.70	120.57
(N4)(C1)(C2)	109.26	110.00
(N1)(C5)(O1)	110.72	109.90
(N2)(C6)(O1)	109.34	109.91
(N3)(C8)(O2)	110.40	110.64
(N4)(C7)(O2)	110.58	110.65
(C5)(O1)(C6)	116.81	116.15
(C7)(O2)(C8)	115.88	115.20
Selected torsion angles	Selected torsion angles, grad	
(M1)(N1)(C5)(O1)	44.25	48.33
(M1)(N2)(C6)(O1)	48.91	48.33
(M1)(N3)(C8)(O2)	41.41	42.19
(M1)(N4)(C7)(O2)	43.94	42.16
(N1)(C5)(O1)(C6)	81.29	79.98
(N2)(C6)(O1)(C5)	83.97	79.98
(N3)(C8)(O2)(C7)	73.98	74.34
(N4)(C7)(O2)(C8)	75.60	74.32
(N1)(C2)(C1)(N4)	43.58	38.93

Table 2. Standard thermodynamic parameters of Fe^{III} and Co^{III} complexes with 1,8-dioxa-3,6,10,13-tetraaza-cyclotetradecanetetrathione-4,5,11,12, H_2O and OH^- group.

M	Standard thermodynamic parameters of formation			Standard thermodynamic parameters of atomization		
	$\Delta H^0_{f,298}$, kJ/mole	$S^0_{f,298}$, J/mole·K	$\Delta G^0_{f,298}$, kJ/mole	ΔH^{at}_{298}, kJ/mole	S^{at}_{298}, J/mole·K	ΔG^{at}_{298}, kJ/mole
Fe	-74.5	794.8	8.8	13058.20	4066.76	11845.70
Co	-126.8	778.4	-37.7	13118.63	4082.16	11901.54

case of Co^{III} this distinction is considerably larger (54.02 kJ), and spin isomerism is impossible here.

The data of quantum-chemical calculation of values of standard thermodynamic parameters of macrotetracyclic compounds (**I**) under examination are presented in Table 2. As may be seen, $\Delta G^0_{f,298}$ value for Fe^{III} complex is positive, while for Co^{III} complex $\Delta G^0_{f,298}$ value is negative; this circumstance is indicative for cobalt(III) complex which is more stable in comparison with iron(III) complex. It is characteristic that $\Delta H^0_{f,298}$ values of both the macrotetracyclic compounds are negative; in addition, $S^0_{f,298}$ values of given complexes are rather close to each other (~ 800 J/mole·K).

According to the calculation data, heteroligand Fe^{III} and Co^{III} complexes with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetrathione-4,5,11,12, H_2O and OH^- have rather considerable electric dipole moments – 4.22 and 3.64 Debye units, respectively. Figures 1, 2 show, that both complexes are asymmetric and have no symmetry elements. Besides, more high value of electric dipole moment is reached for Fe^{III} complex, the assymmetry of which, judging by values of valence angles and bonds lengths (Table 1), is most pronounced.

Conclusions

Heteroligand macrotetracyclic Fe^{III} and Co^{III} complexes with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecanetetrathione-4,5,11,12, H_2O and OH^- ions, considered in the given paper, have quasi-octahedral coordination of donor centers (four nitrogen atoms of 14-membered tetraazaheterocyclic ligand, oxygen atoms of H_2O and OH^- ligands) around of central M^{III} ion. In confirmity to theoretical expectations, MN_4 chelate unit is practically plane. Besides, additional six-membered cycles containing N–C–O–C–N grouping formed as a result of template "stitching", is not in one plane with (NNNN) donor centers; it has been rather considerably inclined to flatness indicated; the degree of this slope for each of these cycles in the same complex is different. The each of these additional six-membered cycles is extremely distorted – there are no set even of four atoms arranged in the same flatness, in each of them, and no of these additional six-membered cycles is itself plane. The complexes considered have no elements of symmetry and rather considerable electric dipole moments [4.22 Debye units (Fe) and 3.64 Debye units (Co)]. In addition, in the Co^{III} complex there are two intra-molecular hydrogen bonds between oxygen atom of hydroxo group and hydrogen atoms of iminogroups whereas in the Fe^{III} complex such bonds are absent.

Both metalmacrotetracyclic compounds (**I**) considered are low-spin complexes; basic state in the case of Fe^{III} complex is spin doublet, and of Co^{III} complex - spin singlet.

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