

DFT B3LYP Quantum–Chemical Calculation of Molecular Structures of (6.6.6)Macrotricyclic M^{II} Complexes with (N,N,N,N)–Coordinating Ligand Formed in the M^{II}–Hydrazinomethanethiohydrazide–Propanone Triple Systems

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Using DFT B3LYP method with 6-31G(d) basis set and the Gaussian 98 program, a calculation of geometric parameters of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes with the tetradentate ligand – 4,6,6-trimethyl-2,3,7,8-tetraazanonen-3-dithiohydrazide-1,9 with NNNN-coordination of donor centres formed as a result of template processes in the M^{II}–hydrazinomethanethiohydrazide–propanone triple systems, was carried out. The bond lengths and angles between various atoms in each of above-mentioned complexes is presented. It is noted that the additional 6-membered metalchelate cycle formed as a result of template “stitching”, is not planar and is turned round with respect to the two 6-membered cycles on rather considerable angle; moreover, none of the chelate cycles in these complexes is plane.

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

Introduction

Previously we have reported^[1-3] on the template syntheses in the M^{II} ion–hydrazinomethanethiohydrazide [H₂N–NH–C(=S)–NH–NH₂]–propanone H₃C–C(=O)–CH₃ triple systems proceeding into metalhexacyanoferrate(II) gelatin-immobilized matrix implants (MHF-GIM, M = Co, Ni, Cu). Some details concerning the coordination of ligands formed as a result of such syntheses (what is known as chelating agent), to the corresponding metal ion were also established. According to mass-spectroscopy data, among other products of such synthesis, (6.6.6)macro-tricyclic metalcomplexes (I) with 4,6,6-trimethyl-2,3,7,8-tetraazanonen-3-dithiohydrazide-1,9, are present in small amounts. Such metalmacrocylic species are formed in the corresponding GIM according to the probable general reaction (1)

The three-dimensional structure of metalmacrocylic compounds (I) is an open question up to now because attempts to obtain their crystals suitable for X-ray diffraction analysis, from gelatin matrix, were unsuccessful. In this connection, it appears expedient to carry out calculation of geometrical parameters of metalcomplexes formed in the systems under examination, using any of the modern quantum-chemical

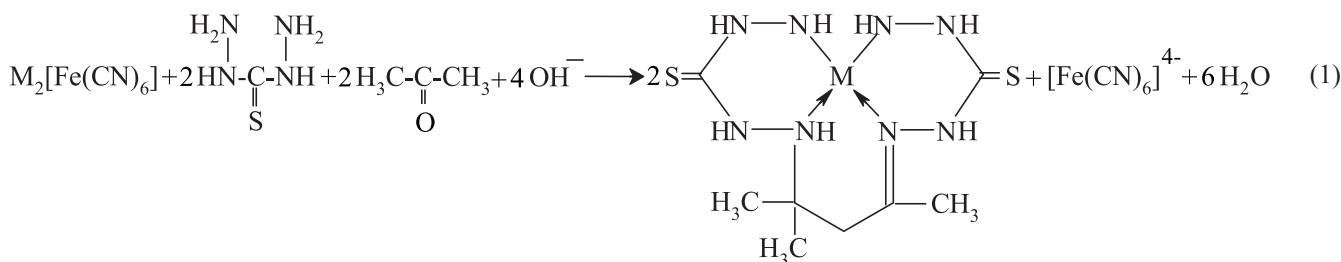
methods able to provide independent objective data about their parameters. One such method is the hybrid method of density functional theory – DFT B3LYP; the present paper is devoted to enumeration and discussion of results of quantum-chemical calculation using this method.

Method

The B3LYP 6-31G(d) method, which is the hybrid DFT method using Becke function (1988) including Slater exchange, by beginning with amendment including density gradient, and correlation functional of Lee, Yang and Parr, which includes local and non-local terms,^[4,5] was used by us for calculations. The energy values E were calculated according to the equation:

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

where V is nuclear energy of repulsion, $\langle hP \rangle$ – one-electronic (kinetic + potential) energy, $1/2 \langle PJ(P) \rangle$ – energy of electron repulsion, $EX[P]$ – exchange functional; $EC[P]$ – correlation functional. The 6-31G(d) basis, set where each inner atom orbital (AO) is described by six functions of Gaussian 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



co-ordinates of atoms. Each equilibrium structure corresponding to points of a minimum on surfaces of potential energy, had only material values of frequencies. No limitation in symmetry was imposed on calculated complexes. All calculations were performed using the Gaussian 98 program.^[6] The time required to complete the quantum-chemical calculations of complexes studied was 6-7 months.

Results and Discussion

The molecular structures of given template complexes obtained as a result of quantum-chemical calculations, are presented on the Figures 1-6. As may be seen, the complexes under examination have quasi-tetrahedral coordination of donor centers around M^{II} central ion. According to the data of these calculations, metalmacrotricyclic coordination compounds (**I**) of Mn^{II} , Co^{II} and Ni^{II} are high-spin complexes (spin multiplicity of basic state is 6, 4 and 3, respectively). The basic states of Cu^{II} and Zn^{II} compounds are spin doublet and spin singlet, respectively. At the same time it is particularly interesting that the Fe^{II} coordination compound with the ligand studied is intermediate-spin, as the spin multiplicity of its ground state is 3. It should be noted in this connection that in the case of the Ni^{II} complex the difference between the energy of the ground state (spin triplet) and the energy of the nearest excited state (spin singlet) is only 0.9 kJ, and, in principle, spin-isomeric coordination compounds may be expected in this case. The data concerning energies of states with various M_s are presented in the Table 1.

As may be seen (Figures 1 - 6), in all compounds of type (**I**) under examination the grouping of four nitrogen

atoms forming the chelate unit MN_4 is not planar. Besides, significantly, the sum of angles $\angle(N1)(N2)(N6)$, $\angle(N2)(N6)(N5)$, $\angle(N6)(N5)(N1)$ and $\angle(N5)(N1)(N2)$, as a rule, is considerably smaller than 360.00° [this sum is equal to 311.1° (Mn), 351.6° (Fe), 326.8° (Co), 309.6° (Ni), 314.7° (Cu) and 294.5° (Zn)]. The distances between neighboring nitrogen atoms in the chelate unit MN_4 are extremely different from each other. It is natural that the MN_4 chelate unit is not planar itself, too – in all cases the sum of valence angles $\angle(N1)(M1)(N2)$, $\angle(N2)(M1)(N6)$, $\angle(N6)(M1)(N5)$ and $\angle(N5)(M1)(N1)$ (VAS) is larger than 360° [376.3° (Mn), 364.3° (Fe), 377.7° (Co), 388.2° (Ni), 384.9° (Cu), 395.8° (Zn)], suggesting quasi-tetrahedral coordination of nitrogen donor atoms around M^{II} . Incidentally, in each of the complexes considered, the four $M-N$ bonds can be divided in two pairs of different lengths; as for distances between neighboring nitrogen atoms in the chelate units and for $\angle NMN$ valence angles, they all differ between themselves (Table 2). Upon going from Mn to Fe , the $M-N$ bond lengths decrease, while from Fe to Co - increase, from Co to Ni – decrease again and from Ni to Zn , in a whole, increase again. The two kinds of $M-N$ bonds indicated are fully expected: one is with «anionic» nitrogen atoms ($N5$) and ($N6$) (shorter), the other is with neutral nitrogen atoms ($N1$) and ($N2$) (longer). At the same time, the distances between M and nitrogen atoms ($N3$), ($N4$), ($N7$) and ($N8$) are relatively large – 285-305 pm (Table 2) suggesting only very weak interaction. All the additional six-membered metalcycles formed as a result of template “stitching”, are extremely distorted – there are no sets

Table 1. Relative energies in the ground and in the excited states with various M_s values in metalmacrotricyclic compounds of type (**I**).

M^{II}	Electron configuration	Relative energies for states with various spin multiply M_s , kJ/mol*					
		1	2	3	4	5	6
Mn^{II}	$3d^5$	-	111.6	-	51.7	-	0
Fe^{II}	$3d^6$	82.8	-	0	-	9.3	-
Co^{II}	$3d^7$	-	10.3	-	0	-	145.8
Ni^{II}	$3d^8$	0.9	-	0	-	-	-
Cu^{II}	$3d^9$	-	0	-	151.1	-	-
Zn^{II}	$3d^{10}$	0	-	155.8	-	-	-

* “ - “ non-existing spin states for given M^{II} .

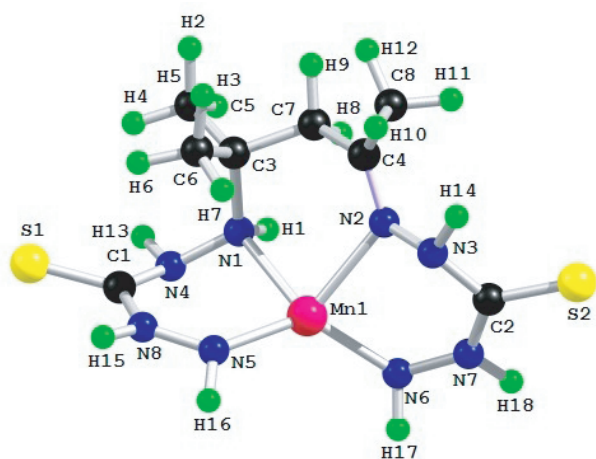


Figure 1. Three-dimensional structure of the Mn^{II} complex of type (**I**), front view.

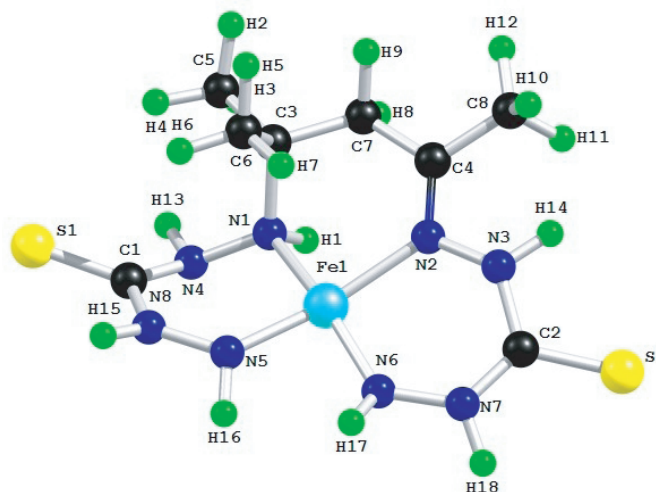


Figure 2. Three-dimensional structure of the Fe^{II} complex of type (**I**), front view.

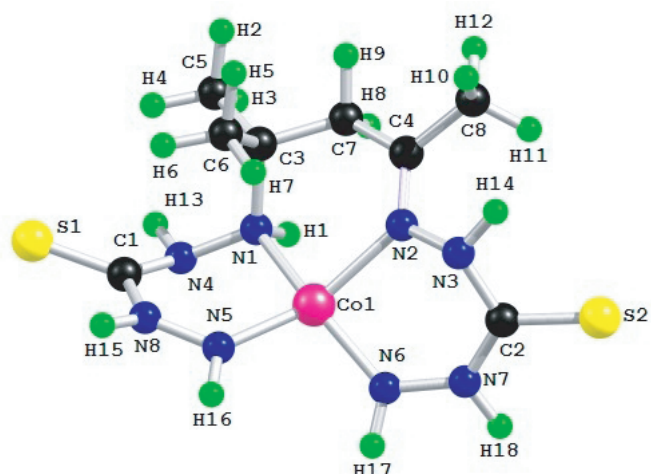


Figure 3. Three-dimensional structure of the Co^{II} complex of type (I), front view.

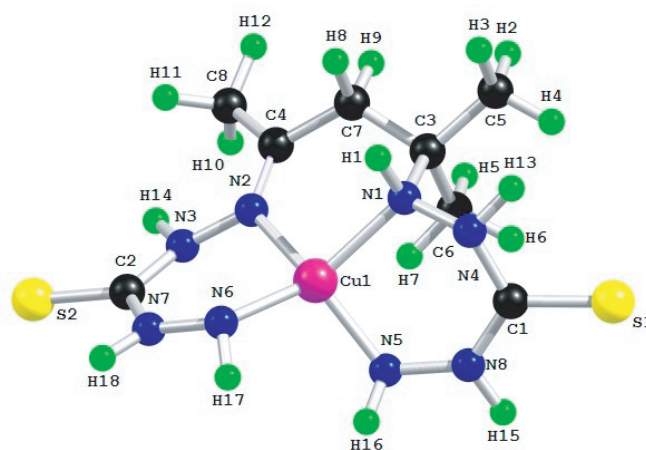


Figure 5. Three-dimensional structure of the Cu^{II} complex of type (I), front view.

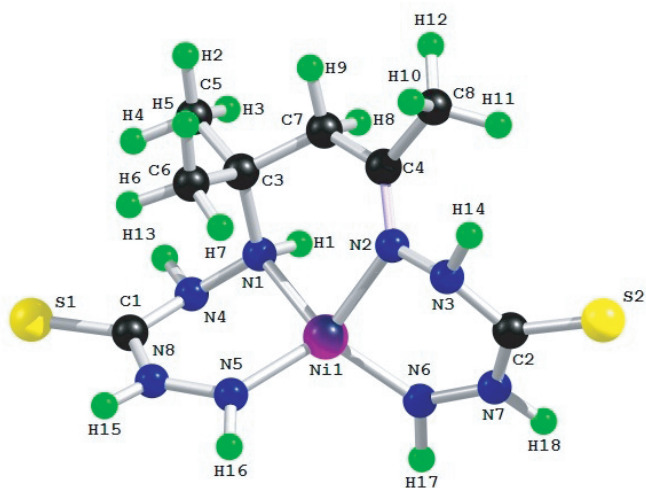


Figure 4. Three-dimensional structure of the Ni^{II} complex of type (I), front view.

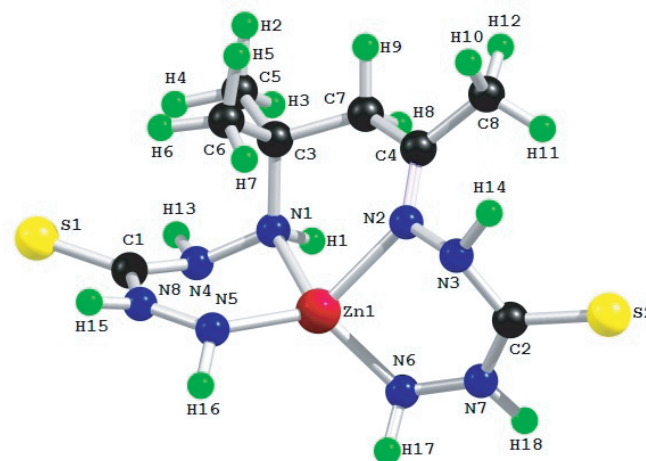


Figure 6. Three-dimensional structure of the Zn^{II} complex of type (I), front view.

even of four atoms arranged in the same plane, in any of them. At the same time, any of these additional six-membered cycles is not itself planar – the (C7) carbon atom contained in it, is deflected from the N–CH₂–CH₂ group by a considerable angle [torsion angles $\angle(C7)(C3)(N2)(C4)$ and $\angle(C7)(C4)(N1)(C3)$, which may be considered as a measure of this deflection, are 37.2° and 38.4° in the case of Mn^{II} complex, 11.6° and 28.7° in the case of the Fe^{II} complex, 17.2° and 34.0° in the case of the Co^{II} complex, 19.6° and 34.0° in the case of Ni^{II} complex, 20.4° and 34.4° in the case of the Cu^{II} complex and 16.8° and 32.7° – in the case of Zn^{II} complex. It is noteworthy that in the case of the Mn^{II} complex, the values of given torsion angles are practically equal whereas in the case of all the other complexes studied, they differ essentially from each other.

In the free ligand, 4,6,6-trimethyl-2,3,7,8-tetraazaanon-3-dithiohydrazide-1,9, the N–N-bond lengths (N1)(N4), (N2)(N3), (N6)(N7) and (N5)(N8) are 141.7, 136.9, 141.8 and 141.7 pm, N–N distances between neighboring nitrogen atoms (N1)(N2), (N2)(N6), (N6)(N5) and (N5)(N1) – 324.3, 277.4, 308.8 and 286.5 pm, respectively. As may be seen from these data, the values of N–N-bond lengths in the free ligand are similar to the ones in the complexes under examination,

whereas the values of N–N distances between neighboring nitrogen atoms (N1)(N2), (N2)(N6), (N6)(N5) and (N5)(N1) are appreciably different from similar parameters for the given complexes.

The data of quantum-chemical calculation of values of standard thermodynamic parameters of metalmacrotricyclic compounds (I) under examination are presented in the Table 3. As may be seen, $\Delta G_{f,298}^0$ values for almost each of these complexes are large and considerably positive, which is an indication on their comparatively small stability. In addition, the largest $\Delta G_{f,298}^0$ value was calculated for the Fe^{II} complex, and the smallest one for Zn^{II} complex. Besides, thermodynamic characteristics of the considered complexes differ only slightly from the values for the free ligand 4,6,6-trimethyl-2,3,7,8-tetraazaanon-3-dithiohydrazide-1,9 (see Table 3).

According to the data of our calculations, all complexes with 4,6,6-trimethyl-2,3,7,8-tetraazaanon-3-dithiohydrazide-1,9 examined here have extremely high electric dipole moments – 3.75 (in the case of the Mn^{II} complex), 6.29 (Fe^{II} complex), 5.20 (Co^{II} complex), 5.96 (Ni^{II} complex), 6.12 (Cu^{II} complex) and 5.24 (Zn^{II} complex)

Table 2. M–N and N–N bond lengths and ∠NMN valence angles in metalmacrotricyclic compounds of type (I).

M	Mn	Fe	Co	Ni	Cu	Zn
M–N bond lengths, pm						
(M1)(N1)	227.9	202.3	212.0	208.4	202.9	213.3
(M1)(N2)	224.5	200.9	206.9	202.7	203.6	209.7
(M1)(N5)	198.2	185.2	188.3	185.8	188.9	190.3
(M1)(N6)	199.3	184.9	189.1	186.7	188.8	191.2
Non-bonding M–N distances, pm						
(M1)(N3)	287.5	293.9	290.7	284.1	287.8	284.4
(M1)(N4)	303.5	294.0	297.3	292.5	287.4	290.0
(M1)(N7)	301.6	291.2	293.7	292.0	287.8	291.8
(M1)(N8)	304.5	291.7	293.0	293.0	290.7	291.7
∠NMN valence angles, grad						
∠(N1)(M1)(N2)	85.0	91.9	92.2	92.0	93.9	87.9
∠(N2)(M1)(N6)	85.4	92.7	90.5	90.0	92.7	90.0
∠(N6)(M1)(N5)	128.6	88.0	103.7	114.9	103.5	125.5
∠(N5)(M1)(N1)	87.3	91.7	91.3	91.1	94.8	93.3
N–N bond lengths, pm						
(N1)(N4)	144.4	144.4	144.1	143.9	143.6	144.1
(N2)(N3)	139.0	138.7	139.7	139.6	137.3	140.7
(N6)(N7)	139.8	139.1	139.0	139.1	140.0	140.1
(N5)(N8)	139.6	139.5	139.1	138.9	140.1	139.9
N–N distances between neighboring nitrogen atoms in the chelate unit MN ₄ , pm						
(N1)(N2)	305.6	289.6	301.8	295.7	297.0	293.7
(N2)(N6)	287.9	279.3	281.5	275.6	284.2	283.9
(N6)(N5)	358.2	257.2	296.8	314.0	296.6	339.1
(N5)(N1)	297.9	278.3	286.6	281.8	288.7	294.0

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

M	Standard thermodynamical parameters of formation			Standard thermodynamical parameters of atomization		
	$\Delta H_{f, 298}^0$, kJ/mole	$S_{f, 298}^0$, J/mole·K	$\Delta G_{f, 298}^0$, kJ/mole	$\Delta H_{at, 298}^0$, kJ/mole	$S_{at, 298}^0$, J/mole·K	$\Delta G_{at, 298}^0$, kJ/mole
Mn	700.7	746.4	976.5	13575.8	4314.9	12289.3
Fe	763.9	729.4	1043.3	13648.5	4338.7	12354.9
Co	717.4	738.1	995.1	13703.2	4329.1	12412.5
Ni	728.8	737.1	1006.7	13696.6	4332.7	12404.8
Cu	626.8	729.9	907.8	13707.5	4324.1	12418.2
Zn	611.3	720.9	897.6	13515.4	4328.0	12225.0
Free ligand	659.6	739.9	966.7	13772.3	4377.1	12467.2

Debye units. As may be seen, upon going from Mn to Fe the electric dipole moment increases, while from Fe to Co it decreases, from Co to Cu – increases again and from Cu to Zn – decreases again. The large values of dipoles for the complexes indicated are perfectly understandable because, as it may be seen on Figures 1 - 6, all they are distinctly asymmetric. It is extremely interesting that the electric dipole moment reaches the maximal value in the Fe^{II} complex, for which, judging by values of valence angles and bonds lengths (Table 2), this asymmetry must be less pronounced. Also, it is interesting that the character of change of electric dipole moment values for these complexes in the Mn–Zn series is reverse in comparison with the character of change of values of M–N bond lengths (see above).

Conclusions

As may be seen from the aforesaid, all macrotricyclic M^{II} complexes with 4,6,6-trimethyl-2,3,7,8-tetraazanonon-3-dithiohydrazide-1,9 considered here have quasi-tetrahedral coordination of the four nitrogen donor atoms to the central M^{II} ion. Significantly, the values of sum of valence angles ∠(N1)(M1)(N2), ∠(N2)(M1)(N6), ∠(N6)(M1)(N5) and ∠(N5)(M1)(N1) formed by the corresponding metal with two neighboring nitrogen atoms, surpass 360° for all M^{II} ions considered here. At the same time, the sum of non-valence angles ∠(N1)(N2)(N6), ∠(N2)(N6)(N5), ∠(N6)(N5)(N1) and ∠(N5)(N1)(N2), as a rule, is considerably smaller than 360° (in the case of Zn – even smaller than 300°), which is

additional evidence of quasi-tetrahedral orientation of donor centers of the polyamine ligand around M^{II} . The character of change of M–N bond lengths in the Mn–Zn series, altogether, coincides with character of change of radii of divalent ions in the same series; nevertheless, the N–N bond lengths in all these complexes are practically equal. Minimal values of M–N bond lengths are reached in the case of the Ni^{II} complex, with maximal ones in the case of Mn^{II} . All these complexes are strongly asymmetric and have no elements of symmetry; this fact is in full agreement with the large values of their electric dipole moment (3.7 – 6.3 Debye units). These and similar data are of certain interest for structural coordination chemistry of macrocyclic complexes, especially as experimental determination of molecular structures of compounds considered in this paper is so far extremely difficult.

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