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Comparative Stability of Isomeric (565)Macrotricyclic Chelates of 3*d*-Elements Formed in the Systems M(II)–Thiosemicarbazide–Formaldehyde According to DFT B3LYP Data

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Abstract—Comparative stability of three types of (565)macrotricyclic chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with chelate nodes MN_2S_2 and MN_4 have been analyzed by means of hybrid density functional method B3LYP with the 6-31G(d) basis set using GAUSSIAN-09 software. These chelates may potentially be formed in template interaction between gelatin-immobilized hexacyanoferrate(II) of respective metal ions M(II), thiosemicarbazide $H_2N–HN–C(=S)–NH_2$, and formaldehyde $H_2C=O$. It has been demonstrated that for all M(II) considered, the complex with chelate nodes MN_2S_2 is more stable. Key structural parameters of the complexes (bond lengths, bond and torsion angles) are presented. It is noted that pseudotetrahedral coordination of ligand donor centers around M(II) is typical for Mn(II), Co(II), Cu(II), and Zn(II), whereas for Fe(II) and Ni(II) it is almost planar. Values of standard enthalpy $\Delta H^0_{f,298}$ and standard Gibbs energy $\Delta G^0_{f,298}$ are positive for nearly all the complexes studied.

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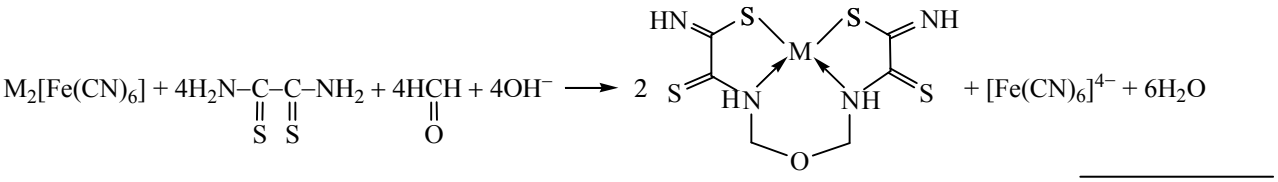
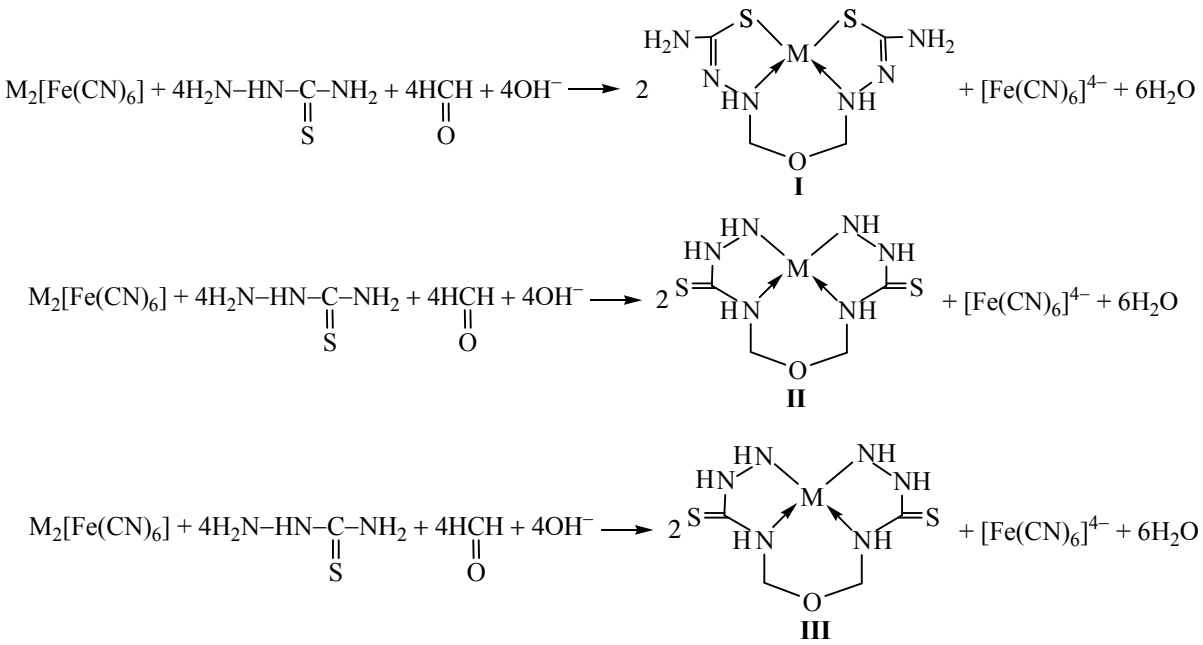
In our previous paper [1] we reported on quantum-chemical computational investigation of the (565) macrotricyclic chelates of some M(II) ions of 3*d*-elements. Such chelates may be formed in template reactions between M(II), ethanebis(thioamide) $H_2N–C(=S)–C(=S)–NH_2$, and formaldehyde $H_2C(=O)$ in matrix implants based on gelatin-immobilized metal hexacyanoferrate(II) (metal M = Mn, Fe, Co, Ni, Cu, Zn).



Theoretically, similar template process may be possible in ternary systems containing another (N,S)-ligson, thiosemicarbazide $H_2N–HN–C(=S)–NH_2$, instead of ethanebis(thioamide). However, in the case of thiosemicarbazide three isomeric (565)macrotricyclic chelates (**I, II, III**) can be formed; in **I** the ligand is coordinated with M(II) through two sulfur and two nitrogen atoms, whereas in **II, III** the coordination through four nitrogens takes place.

Various derivatives of thiosemicarbazide have been well recognized as ligand synthones [2, 3]; however, there is no information of application of thiosemicarbazide itself to template processes and on complex formation or template processes in systems M(II)-thiosemicarbazide-formaldehyde. Thus, whether all of metal chelates **I–III** may be formed in such systems, or one of the types will appear exclusively, has been an open question so far. To investigate the possibility of



the template process in the M(II)-thiosemicarbazide-formaldehyde system and the process direction, it is reasonable to run quantum-chemical calculation of the parameters of metal complexes **I–III** applying the method described in [1, 4–7]. This computational method gives independent data on the complexes full energy (E), standard enthalpy ($\Delta H^0_{f,298}$), standard entropy ($S^0_{f,298}$), and standard Gibbs energy ($\Delta G^0_{f,298}$) of the complexes formation, as well as geometrical parameters of structures (bond lengths, bond and torsion angles).

Quantum-chemical data on full energy E of (565)macrotricyclic complexes **I–III** of metal ions M(II) with the ground state spin multiplicity M_S, corresponding to the energy minimum, are collected in Table 1. Table 2 presents the data of ground and excited states with various spin multiplicity. It is clear that for all metals considered E(**III**) > E(**II**) > > E(**I**) is valid, with E(**I**), E(**II**), and E(**III**) being full energies of complexes of types **I**, **II**, and **III**, respectively, with accounting for the zero oscillations energy. For all M(II) studied, difference between E(**I**) and E(**II**), or

Table 1. Full energy E with accounting for the zero oscillations energy for the complexes **I**, **II**, and **III,** for different M(II) in the gas phase[a]

M(II)	E(**I**)	E(**II**)	E(**III**)
Mn(II)	–2509.332262 [0.0]	–2509.257282 [196.8]	–2509.261463 [185.9]
	(M_S = 6)	(M_S = 6)	(M_S = 6)
Fe(II)	–2622.006793 [0.0]	–2621.950676 [147.3]	–2621.946687 [157.8]
	(M_S = 3)	(M_S = 3)	(M_S = 3)
Co(II)	–2741.044730 [0.0]	–2740.978351 [174.3]	–2740.975149 [182.7]
	(M_S = 4)	(M_S = 2)	(M_S = 4)
Ni(II)	–2866.555801 [0.0]	–2866.500066 [146.3]	–2866.498800 [149.6]
	(M_S = 1)	(M_S = 1)	(M_S = 1)
Cu(II)	–2998.684112 [0.0]	–2998.618700 [171.7]	–2998.602295 [214.8]
	(M_S = 2)	(M_S = 2)	(M_S = 2)
Zn(II)	–3137.532260 [0.0]	–3137.470968 [160.9]	–3137.462931 [182.0]
	(M_S = 1)	(M_S = 1)	(M_S = 1)

[a] Values without brackets correspond to full energy in Hartree units; values in brackets are relative energies in kJ mol^{-1}, with 0.0 corresponding to full energy of the type **I** complex with the lowest E.

E(**I**) and E(**III**) is fairly large (> 50 kJ mol^{-1}), thus, in any of the considered systems the formation of a single macrotricyclic complex, **I**, is most favorable. Although the data on the respective stabilities of chelates **II** and **III** concern their gaseous state, taking into account special features of the macrocyclic ligand and M(II) ions, the result should not drastically change in the case of the condensed state. For instance, it follows from the results presented in [4, 5] that if the full energies difference of the isomeric complexes in the gaseous phase is more than 50 kJ mol^{-1}, it is at least positive in the condensed phase. Indeed, the results of our quantum-chemical calculations of the same complexes with the PCM method [8] for the condensed state are essentially the same as the qualitative energy relations of the complexes presented in Table 1. However, PCM method does not allow geometry optimization which affects much the calculated energy parameters, thus, the full energies of the complexes in the condensed phase obtained by PCM seem less reliable than the corresponding data obtained with DFT B3LYP/6-31G(d) for the gaseous phase. Furthermore, according to [9, 10] a so-called orbital electronegativity may be used as a measure of the ability of the metal ion to complex formation. The orbital electronegativity for the studied M(II) ions equals 13.59, 0.66 (Mn), 14.11, 0.69 (Fe), 14.47, 0.52 (Co), 15.00, 0.29 (Ni), 15.44, –0.56 (Cu), and 15.82, –1.02 (Zn) eV in gaseous phase and in aqueous solution, respectively [10]. The orbital electronegativity values for the gaseous phase are typical of hard Pearson acids; for such acids the coordination to highly electronegative donor atoms, four nitrogen atoms (NNNN) in the considered case, should be favorable. When forming complexes in solution, M(II) are Pearson acids of intermediate strength, and coordination to two nitrogen and two sulfur atoms (NSSN) seems more probable. This means that if (as it is in the studied case) even in the gaseous phase (NSSN)-coordination is preferred over the (NNNN)-type, it should be even more favorable in the condensed phase (solutions, matrix-immobilized solids). Standard thermodynamic parameters of the studied metal complexes (Table 3) also indicate the higher stability of the type **I** complexes as compared with that of types **II** and **III**. It is to be seen that standard enthalpy of formation ($\Delta H^0_{f,298}$) and standard Gibbs energy of formation ($\Delta G^0_{f,298}$) are positive for almost all studied metal complexes **I–III,** being rather high in absolute value in many cases. Also, standard entropy of formation ($S^0_{f,298}$) of compounds **I–III** is high (hundreds of J mol^{-1} K^{-1}). However, all the mentioned thermodynamic parameters are higher for type **I** complex than those of types **II**, **III** complexes, for any given metal ion M(II).

Table 2. Relative energy of the ground and the excited states with different spin multiplicity M_S for the complexes **I**, **II**, and **III,** for different M(II) in the gaseous phase, kJ mol^{-1} [a]

M(II)	I	II	III
Mn(II)	M_S = 2 (144.6)	M_S = 2 (87.2)	M_S = 2 (115.8)
	M_S = 4 (65.8)	M_S = 4 (28.8)	M_S = 4 (51.3)
	M_S = 6 (0.0)	M_S = 6 (0.0)	M_S = 6 (0.0)
Fe(II)	M_S = 1 (144.4)	M_S = 1 (133.3)	M_S = 1 (121.6)
	M_S = 3 (0.0)	M_S = 3 (0.0)	M_S = 3 (0.0)
	M_S = 5 (19.2)	M_S = 5 (37.1)	M_S = 5 (10.2)
Co(II)	M_S = 2 (24.3)	M_S = 2 (0.0)	M_S = 2 (9.1)
	M_S = 4 (0.0)	M_S = 4 (3.3)	M_S = 4 (0.0)
Ni(II)	M_S = 1 (0.0)	M_S = 1 (0.0)	M_S = 1 (0.0)
	M_S = 3 (10.5)	M_S = 3 (11.4)	M_S = 3 (21.5)
Cu(II)	M_S = 2 (0.0)	M_S = 2 (0.0)	M_S = 2 (0.0)
	M_S = 4 (304.2)	M_S = 4 (158.3)	M_S = 4 (137.6)
Zn(II)	M_S = 1 (0.0)	M_S = 1 (0.0)	M_S = 1 (0.0)
	M_S = 3 (291.2)	M_S = 3 (183.8)	M_S = 3 (242.6)

[a] In all cases 0.0 stands for the full energy of the complex with spin multiplicity corresponding to the lowest energy.

The calculation of **I–III** structural parameters unexpectedly reveals that all complexes are non-coplanar and asymmetric, with an only mirror plane. Nevertheless, as presumed, structural types of complexes **II** and **III** are similar, while type **I** complex is different. The major difference is that structures of types **II** and **III** complexes are planar or close to planar, with the sum of bond angles in the MN_4 chelate node normally less than 360°, while type **I** complexes are pseudotetrahedral, with the sum of bond angles in the node MN_2S_2 more than 360°. Note that the mentioned behavior is quite rare, and we are not aware of it to the very best of our knowledge summarized in the recent review on structural peculiarities of macrotricyclic complexes with chelate nodes MN_2S_2 and MN_4 [12]. Some examples of the molecular structures of the mostt stable complexes, those of type **I**, are shown in Figs. 1–3. The calculated structural parameters, bond lengths, bond and torsional (dihedral) angles, for complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) of this type are presented in Table 4. As seen from this table, the sum of bond angles in the

Table 3. Standard enthalpy, entropy, and Gibbs energy of formation for macrotricyclic metal complexes **I–III**

Type of complex	M(II)	$\Delta H^0_{f,298}$, kJ mol^{-1}	$S^0_{f,298}$, J mol^{-1} K^{-1}	$\Delta G^0_{f,298}$, kJ mol^{-1}
I	Mn(II)	198.4	591.3	338.6
	Fe(II)	–17.5	575.3	126.1
	Co(II)	128.8	600.2	265.8
	Ni(II)	248.7	571.2	394.3
	Cu(II)	136.7	573.9	282.5
	Zn(II)	109.5	566.0	260.3
II	Mn(II)	395.8	610.5	530.3
	Fe(II)	130.1	595.6	267.6
	Co(II)	301.1	583.8	443.0
	Ni(II)	394.5	584.4	536.2
	Cu(II)	308.5	583.1	451.6
	Zn(II)	270.4	582.5	416.2
III	Mn(II)	385.3	613.2	519.1
	Fe(II)	139.1	569.0	284.6
	Co(II)	311.1	600.9	447.9
	Ni(II)	396.3	557.7	545.9
	Cu(II)	352.8	592.5	493.1
	Zn(II)	291.3	568.8	441.2

MN_2S_2 chelate node equals 377.5° for Mn(II), 406.5° for Co(II), 365.6° for Cu(II), and 382.9° for Zn(II); only for complexes of Fe(II) and Ni(II) this sum is close to 360° (359.9° and 360.1°, respectively). The group of nitrogen and sulfur donor atoms is non-coplanar in most cases as well, as the sum of nonbond angles (NBAS) is significantly less than 360° for four complexes among six. In this context, Co(II) complex attracts attention, as in this case bond angles sum for the MN_2S_2 chelate node exceeds 400° and is closer to bond angles sum for perfect tetrahedral orientation of the donor atoms relative to the central atom (437°52') than to that for planar orientation (360°00'); NBAS is by almost 80° (!) smaller than that in planar tetragon. At the same time, in all type **I** complexes the mentioned angles are different from one another. M–N bonds are longer than M–S bonds in the studied complexes. It is interesting that in Fe(II) and Ni(II) complexes the bond lengths are equal in pairs, while in other complexes they are all different. In the series of the studied metal ions, the bond lengths changs as follows: Mn > Fe < Co > Ni < Cu < Zn.

Even though the chelant donor centers are oriented pseudotetrahedrally with respect to M(II) in the majority of the complexes considered in this work, 5-membered chelate cycles containing N and S donor atoms are most often quasiplanar, as their bond angles sum (BAS^{51} and BAS^{52}) either is equal to the sum of inner angles in a planar pentagon, 540°, [for Ni(II) complex], or are relatively close to this value [for Fe(II), Co(II), and Cu(II) complexes] (Table 1). The bond angle values show that BAS^{51} and BAS^{52} are practically the same in the Fe(II) и Ni(II) complexes, whereas in the other complexes these values are different. For instance, in Mn(II) complex, showing the highest difference between the angles sums, BAS^{51} is 531.6° and BAS^{52} equals 519.1°. For the 6-membered cycles, appearing additionally due to template "cross-link" and containing only two donor nitrogen atoms, deviation from coplanarity is more pronounced than for the 5-membered cycles; this is evidenced by the bond angles sum values (BAS^6): 651.2°, 654.1°,

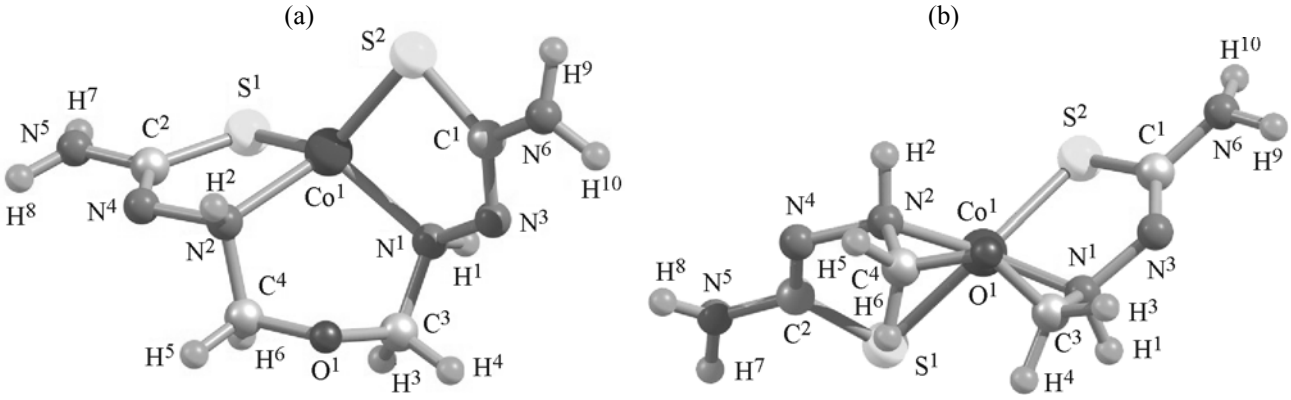


Fig. 1. Three-dimensional structure of Co(II) complex: (a) front view and (b) side view.

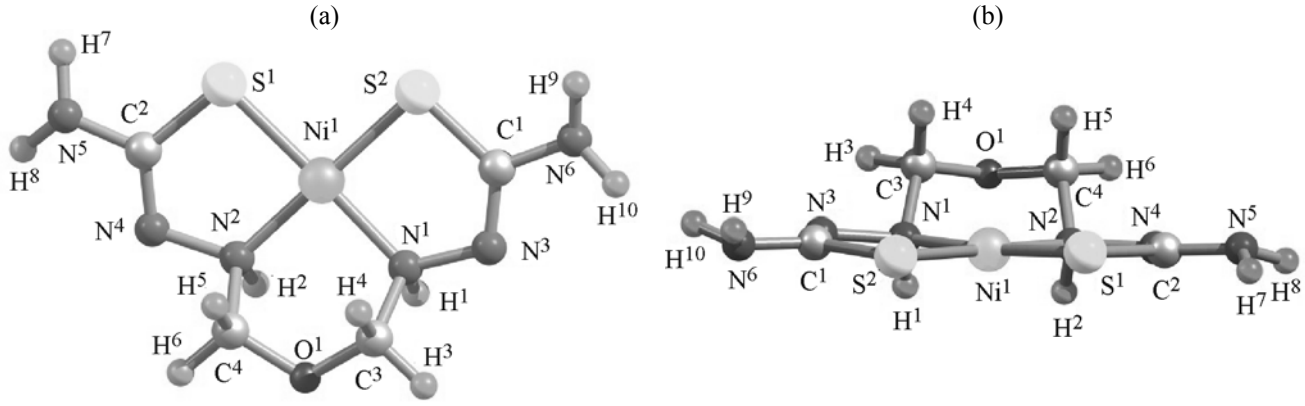


Fig. 2. Three-dimensional structure of Ni(II) complex: (a) front view and (b) side view.

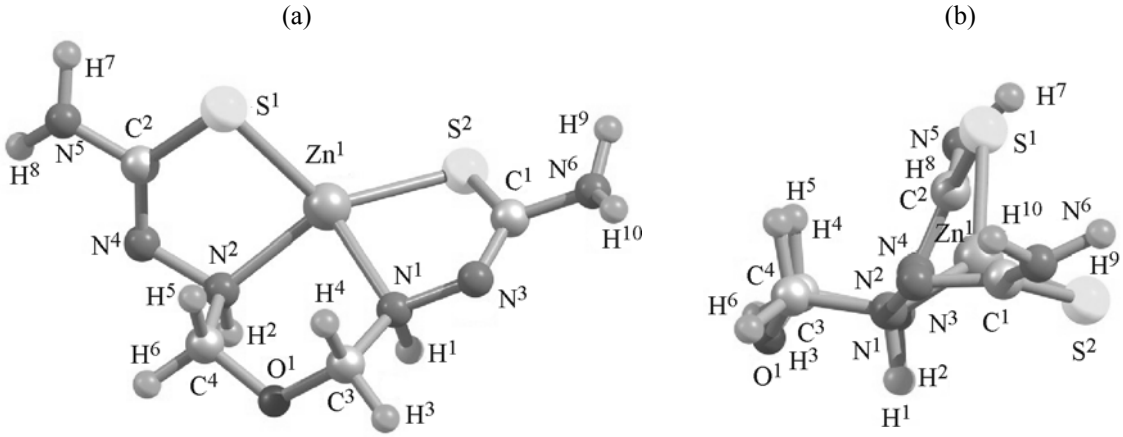


Fig. 3. Three-dimensional structure of Zn(II) complex: (a) front view and (b) side view.

664.9°, 649.2°, 651.4°, and 652.0° in cases of Mn, Fe, Co, Ni, Cu, and Zn, respectively. In all cases BAS[6] values are much less than the sum of the inner angles in a planar hexagon (720°). Interestingly, the least deviation from coplanarity is observed in the case of Co(II) complex, where the deviation from coplanarity of the group of N_2S_2 donor atoms is the highest. It is noteworthy that analogous bond angles out of the chelate cycles, for example, ($S^1C^2N^5$) and ($S^2C^1N^6$), ($N^5C^2N^4$) and ($N^6C^1N^3$), ($C^2N^5H^7$) and ($C^1N^6H^9$) for all the complexes studied are either equal or very close. The same holds for the lengths of the bonds forming those angles (Table 1). Values of the just mentioned parameters are relatively insensitive to the nature of the complex forming ion. For instance, S^1–C^2 bond length equals 177.9, 177.3, 178.2, 176.0, 176.5, and 177.5 pm, and bond angle $S^1C^2N^5$ equals 114.7°, 116.1°, 115.0°, 116.9°, 116.0°, and 115.0° in complexes of Mn, Fe, Co, Ni, Cu, and Zn, respectively. In contrast, the values of torsional (dihedral) angles depends strongly on the nature of complexing metal, and type **I** complexes are dissimilar with respect to this parameter. Some similarity is observed only for complexes of Cu(II) and Zn(II) (Table 1).

The ground states of Mn(II) and Co(II) complexes are spin sextet and spin quartet, respectively; both are high-spin complexes. In the case of Ni(II) complex, the ground state is spin singlet, and the complex is a low-spin one. As expected, the ground states of Cu(II) and Zn(II) complexes are spin doublet and spin singlet, respectively. Spin triplet is characteristic of the Fe(II) complex ground state, and it cannot be classified as either high-spin or low-spin. The energy gaps between the ground state and states of other spin multiplicities for majority of the type **I** complexes are quite large (Table 2). Only in the case of Ni(II) complex the gap between the ground singlet state and the nearest triplet

Table 4. Bond lengths, bond and torsional angles in the type **I** complexes of M(II) formed in the system M(II)– thiosemicarbazide–formaldehyde

M	Mn	Fe	Co	Ni	Cu	Zn
Bond lengths in the chelate node MN_2S_2, pm						
M^1N^1	220.6	201.6	207.4	192.8	201.9	208.5
M^1N^2	222.6	201.6	204.6	192.8	201.9	209.9
M^1S^1	239.7	221.5	228.6	217.8	225.4	229.6
M^1S^2	241.2	221.6	227.0	217.6	226.3	231.7
Selected bonds out of the chelate node, pm						
S^1C^2	177.9	177.3	178.2	176.0	176.5	177.5
S^2C^1	178.3	177.3	177.8	176.0	176.7	178.1
C^2N^4	130.6	130.1	130.7	130.1	130.6	130.7
C^1N^3	130.5	130.1	130.4	130.1	130.5	130.5
N^2N^4	145.0	145.6	144.9	145.3	144.6	144.5
N^1N^3	144.2	145.6	145.1	145.3	144.4	143.7
N^2C^4	149.9	149.1	149.0	149.1	149.0	150.1
N^1C^3	147.5	149.1	148.1	149.1	148.2	147.0
C^4O^1	140.7	140.5	140.7	140.4	140.5	140.7
C^3O^1	140.9	140.5	140.8	140.3	140.6	141.2
C^2N^5	137.2	136.7	136.5	137.0	137.0	137.2
C^1N^6	137.2	136.7	137.0	137.0	137.0	137.3
N^5H^7	101.0	100.9	100.8	101.0	101.0	101.0
N^6H^9	101.0	100.9	100.9	101.0	101.0	101.1
Bond angles in the chelate node MN_2S_2, deg						
$S^1M^1S^2$	131.1	96.8	130.0	92.4	101.5	125.3
$S^2M^1N^1$	79.0	86.0	86.7	87.9	85.7	82.4
$N^1M^1N^2$	86.1	91.1	102.2	92.1	91.8	89.8
$N^2M^1S^1$	81.3	86.0	87.6	87.7	86.6	85.4
Sum of the angles (BAS)	377.5	359.9	406.5	360.1	365.6	382.9
Nonbond angles in the N_2S_2 group, deg						
$S^1S^2N^1$	67.5	85.6	63.0	86.2	81.2	68.1
$S^2N^1N^2$	95.6	94.4	76.7	93.6	93.5	91.1
$N^1N^2S^1$	89.2	94.3	77.0	93.7	92.0	85.9
$N^2S^1S^2$	70.8	85.7	63.4	86.3	81.9	70.4
Sum of the angles (NBAS)	323.1	360.0	280.1	359.8	348.6	315.5
Bond angles in 5-membered chelate ring 1,deg						
$M^1S^1C^2$	99.7	96.3	92.1	95.6	94.1	91.6
$S^1C^2N^4$	129.0	126.1	128.5	125.2	127.2	128.5
$C^2N^4N^2$	113.8	111.9	114.4	111.5	112.8	113.3
$N^4N^2M^1$	113.8	119.5	113.7	120.0	117.7	112.6
$N^2M^1S^1$	81.3	86.0	87.6	87.7	86.6	85.4
Sum of the angles (BAS^{51})	531.6	539.8	536.3	540.0	538.4	531.4

Table 4. (Contd.)

M	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in 5-membered chelate ring 2, deg						
$M^1S^2C^1$	90.3	96.3	92.0	95.4	92.9	99.0
$S^2C^1N^3$	127.5	126.1	128.3	125.3	127.0	127.1
$C^1N^3N^1$	112.3	111.9	113.0	111.6	112.3	111.4
$N^3N^1M^1$	110.0	119.3	115.7	119.6	116.0	110.2
$N^1M^1S^2$	79.0	86.0	86.7	87.9	85.7	82.4
Sum of the angles (BAS^{52})	519.1	539.6	535.7	539.8	533.9	520.1
Bond angles in the additional 6-membered chelate cycle, deg						
$M^1N^2C^4$	110.1	112.9	112.4	110.6	111.1	108.8
$N^2C^4O^1$	112.1	110.6	113.1	110.4	111.2	112.6
$C^4O^1C^3$	116.3	115.8	116.2	115.4	115.7	116.0
$O^1C^3N^1$	109.2	110.7	111.2	110.6	110.1	107.9
$C^3N^1M^1$	117.4	113.0	109.8	110.1	111.5	116.9
$N^1M^1N^2$	86.1	91.1	102.2	92.1	91.8	89.8
Sum of the angles (BAS^6)	651.2	654.1	664.9	649.2	651.4	652.0
Bond angles out of the chelate cycles, deg						
$S^1C^2N^5$	114.7	116.1	115.0	116.9	116.0	115.0
$S^2C^1N^6$	115.4	116.1	115.0	116.8	116.0	115.5
$N^5C^2N^4$	116.3	117.8	128.3	117.9	116.8	116.5
$N^6C^1N^3$	117.1	117.8	128.5	117.9	117.0	117.3
$N^4N^2C^4$	107.4	106.7	108.3	106.6	107.1	107.4
$N^3N^1C^3$	109.7	106.4	109.1	106.0	107.6	111.9
$C^2N^5H^7$	116.6	117.3	118.2	116.8	116.7	116.5
$C^1N^6H^9$	116.3	117.2	117.2	117.0	116.6	116.0
$N^2C^4H^5$	107.1	107.8	109.9	107.6	107.2	106.6
$N^1C^3H^4$	108.1	107.7	108.9	107.5	107.8	108.5
Torsional angles, deg						
$S^1M^1N^1C^3$	30.6	2.2	–78.6	32.8	37.0	37.9
$S^2M^1N^2C^4$	107.6	27.5	–117.1	144.9	128.2	121.3
$M^1N^1C^3O^1$	59.4	62.1	–39.2	65.4	63.9	59.7
$M^1N^2C^4O^1$	–66.4	–62.4	50.7	–64.8	–62.4	–65.1
$M^1S^1C^2N^5$	–166.7	175.5	166.1	178.1	–176.9	–167.3
$M^1S^2C^1N^6$	–157.0	179.7	–166.4	178.6	–170.4	–158.8
$M^1S^1C^2N^4$	15.3	–3.1	–13.5	0.0	5.1	15.1
$M^1S^2C^1N^3$	26.3	1.5	13.1	1.0	12.8	25.1
$S^1C^2N^4N^2$	5.2	0.7	0.6	1.8	3.5	4.8
$S^2C^1N^3N^1$	4.3	3.0	–0.7	1.4	3.3	3.8
$N^1C^3O^1C^4$	–75.9	–74.6	80.5	–71.5	–75.8	–74.0
$N^2C^4O^1C^3$	83.7	74.8	–88.4	70.9	75.5	81.6
$N^5C^2N^4N^2$	–172.8	–177.8	–179.0	–176.2	–174.4	–172.8
$N^6C^1N^3N^1$	–172.4	–175.2	178.8	–176.2	–173.4	–172.2
$N^3N^1C^3O^1$	–174.0	–165.1	87.8	–163.8	–168.0	–171.9
$N^4N^2C^4O^1$	169.3	164.4	177.9	163.2	167.8	172.6

state is smaller (10.5 kJ mol^{-1}). However, as our calculations refer to the gaseous state, in the condensed phase the energy gap will likely increase, and the spin isomerism seems impossible for the studied complexes.

As seen in Figs. 1–3, the studied macrotricyclic chelates have at most a single mirror plane. As the symmetry center is absent in the structures, high dipole moment (μ) is expected. The B3LYP/6-31G(d) calculation give the following dipole moment values: 2.42 (Mn), 3.72 (Fe), 3.73 (Co), 3.17 (Ni), 3.27 (Cu), and 2.34 (Zn) D. The least symmetric chelate of the considered set, Co(II) complex, possessed the highest dipole moment value. It is noteworthy that the more symmetric complex of Fe(II) has almost the same μ as does Co(II) complex.

As shown above, the standard Gibbs energy of formation $\Delta G^0_{f,298}$ is positive and quite high for the type **I** complexes. Thus, their formation from elementary substances is impossible, and the overall process described above is likely to be thermodynamically forbidden in solution or in the solid phase. Likely due to this fact, the type **I** complexes formation under ordinary conditions have never been observed before. However, under special conditions, in the nanoscale-organized systems, like gelatin-immobilized metal hexacyanoferrate(II) matrix implants, the formation of the described complexes seems possible [13].

EXPERIMENTAL

Calculations were performed as in [1, 4–7] using a popular hybrid DFT method, B3LYP with the basis set 6-31G(d), based on the combination of the Hartree-Fock method and the density functional theory [14]; the Becke-Lee-Yang-Parr exchange-correlation potential [15] was used. Calculations were performed using GAUSSIAN-09 software [16]. The correspondence of the found stationary points to the energy minima was proved by calculation of the energy second derivatives over the atom coordinates; all the frequencies were found to be positive. Thermochemical parameters (standard enthalpy of formation, standard entropy of formation, and standard Gibbs energy of formation) were calculated according to [11].

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