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DFT Quantum-Chemical Calculation of the Molecular Structures of (5665)Macrotetracyclic Chelates in the M(II)–4,5-Diaminoacridone–2-[(2-Formylphenyl)amino]benzenecarbaldehyde Systems (M = Mn, Fe, Co, Ni, Cu, Zn)

O. V. Mikhailov[a], * **and D. V. Chachkov**[b]

[a]*Kazan National Research Technological University, Kazan, Tatarstan, 420015 Russia*
[b]*Joint Supercomputer Center, Kazan Branch, Russian Academy of Sciences, Branch of Federal Scientific Center "Research Institute for System Studies of the RAS," Kazan, Tatarstan, 420015 Russia*
**e-mail: ovm@kstu.ru*

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Abstract—The geometries of (5665)macrotetracyclic Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes with the NNNN-coordination of the chelant donor sites and the MN_4 chelate core, which can be formed through template processes in the M(II)–2-[(2-formylphenyl)amino]benzenecarbaldehyde–4,5-diaminoacridone have been calculated by the hybrid DFT OPBE/TZVP method with the Gaussian 09 program package. The bond lengths, bond angles, and selected nonbonded angles in these complexes have been determined. It has been demonstrated that none of the chelate rings is strictly planar although these rings in all complexes, except the Co(II) complex, are pairwise identical. The six-membered rings are more noncoplanar than the five-membered rings. The standard enthalpies, entropies, and Gibbs energies of formation of these compounds have been calculated.

Keywords: density functional theory method, macrocyclic ligands

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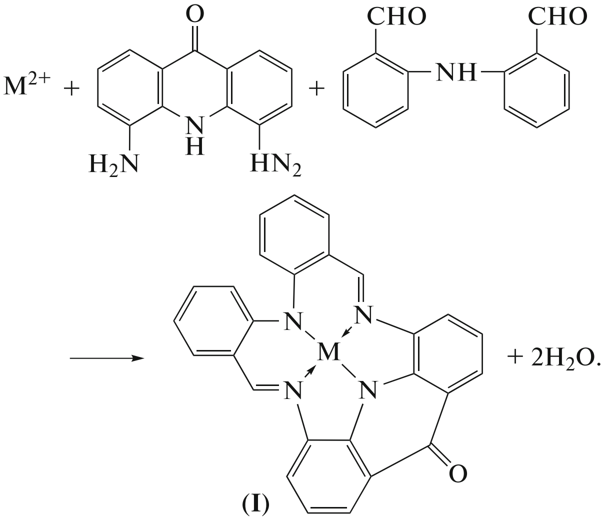
Previously [1–10], we have performed density functional theory (DFT) calculations of 3*d* M(II) chelates (M = Mn, Fe, Co, Ni, Cu, Zn) with macrocyclic ligands containing two five-membered and two six-membered rings of (5665)macrotetracyclic metal chelates. These calculations allow us to conclude that complexes in which the chelate rings with the same number of members share one atom—the central metal atom M, expect Fe(II), Co(II), Ni(II), and Cu(II), with 3,10-dithio-6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclodecatetraene-1,5,7,12 [2, 8]—are noncoplanar. In this context, it is of interest to study the structure of (5665)macrotetracyclic metal chelates in which chelate rings with the same number of atoms share two atoms of general formula [M**L**] (**I**) with a "rigid" 14-membered macrocyclic ligand **L** (chelant) that form, according to [11, 12], in the template reaction between M(II) ions, 2-(2-formylphenyl)aminobenzenecarbaldehyde, and 4,5-diamnioacridone:



(**I**)

The formation of only the [Ni**L**] complex has been reported [11, 12]. The possibility of synthesis of other *d* M(II) complexes by analogous reactions has not been mentioned in the literature. Recent reviews covering the structural chemistry of template complexes have presented no information on such systems [13–15]. Therefore, it seems expedient to perform quantum-chemical calculation of the molecular structures of the [M**L**] metal chelates formed by 3*d*-metal ions by the DFT method in order to elucidate, first, the degree of their noncoplanarity and, second, whether the nickel(II) complex is unique or analogous [M**L**] (**I**) complexes with other 3*d* M(II) ions can also exist. The present paper deals with these issues and discusses specific features of the molecular structures of metal chelates [M**L**].

COMPUTATIONAL DETAILS

Quantum-chemical calculations were performed by the DFT method, combining the common TZVP extended split-valence basis set [16, 17] and the OPBE nonhybrid functional [18, 19], which, as shown in [19–23], in the case of 3*d* elements adequately predicts the relative energy stabilities of high-spin and low-spin states and reliably characterizes key geometric parameters of the molecular structures of metal complexes under consideration. Calculations were performed with the Gaussian09 program package [24]. As in [1–10], the correspondence of the found stationary points to energy minima was proved in all cases by the calculation of second derivatives of energy with respect to atom coordinates. All equilibrium structures corresponding to minima of the potential energy surfaces had only real positive frequency values. Multiplicities 2, 4, and 6 were considered for the Mn(II) and Co(II) complexes, multiplicities 1, 3, and 5 for the Fe(II) complex, multiplicities 1 and 3 for the Ni(II) and Zn(II) complexes, and multiplicities 2 and 4 for the Cu(II) complex. Among the structures optimized at these multiplicities, the lowest-lying structure was selected. Parameters of molecular structures with multiplicities other than 1 were always calculated by the unrestricted Hartree–Fock (UHF) method; parameters of structures with multiplicity 1 were calculated by the restricted Hartree–Fock (RHF) method. At multiplicity 1, the unrestricted method in combination with the option GUESS=Mix was also used; the results thus obtained were always analogous to those obtained by the restricted method. All quantum-chemical calculations were performed at the Joint Supercomputer Center, Kazan Branch, Russian Academy of Sciences–Branch of Federal Scientific Center "Research Institute of System Investigations of the RAS" (http://kbjscc.knc.ru).

RESULTS AND DISCUSSION

According to results of our calculation, complexes **I** can exist for all M(II) ions under consideration (M = Mn, Fe, Co, Ni, Cu, and Zn). The geometrical parameters of the molecular structures of the complexes are presented in Table 1; some of these structures are shown in Figs. 1–3. It is noticeable that they are similar in appearance. On the basis of the above structural formula of chemical compounds **I**, it can be assumed that two M–N bonds, M(1)–N(3) and M(1)–N(4), should be the same in length (*d*), and the other two, M(1)–N(3) and M(1)–N(4), should differ from them in this parameter. The calculation results for five of the six metal chelates confirm this assumption. The only exception is the [Co**L**] complex, in which the *d*(M–N) values of all four bonds are different, and the M(1)–N(3) bond is almost 1 pm longer than the M(1)–N(4) bond. The character of changes in *d*(M–N) values in going from Mn to Zn turns out to be the same: for M(1)–N(1), M(1)–N(3) and M(1)–N(4), they monotonically decrease in going from Mn(II) to Ni(II) and increase in going from Ni(II) to Zn(II). For the M(1)–N(2) bond, the minimum of *d*(M–N) value is observed for the [Co**L**] complex. In almost each of the complexes under consideration, analogous bonds, in particular, N(4)–C(7) and C(3)–N(2), N(1)–C(1) and N(1)–C(8), N(2)–C(4) and N(2)–C(5), and C(3)–C(4) and C(5)–C(6), are equal to each other. This equality is also observed in the cobalt(II) complex. The lengths of the bonds between carbon atoms in "peripheral" six-membered "benzene rings" adjacent to chelate rings (both to the five-membered and six-membered rings) are nearly independent of the nature of the complex-forming M(II) ion, which is predictable. This is also valid for the C(17)–O(1) bond length, which varies in the range of 123.1–123.3 pm.

As follows from Table 1, the MN_4 chelate core in each of the complexes is strictly planar (the sum of the N(1)M(1)N(3), N(3)M(1)N(2), N(2)M(1)N(4), and N(4)M(1)N(1) bond angles (BAS) is 360.0°); in five of them, the N(1)M(1)N(3) and N(4)M(1)N(1), N(3)M(1)N(2) and N(2)M(1)N(4) bond angles are pairwise equal to each other but essentially differ from each other. The difference between these pairs of angles for different M(II) relatively weakly depend on the nature of the 3*d* element M. The exception is Co(II) complex in which all these angles are different. The N_4 group of the donor atoms in the metal chelates is also either perfectly planar (in [Mn**L**], [Fe**L**], [Cu**L**], and [Zn**L**], where the sum of the N(1)N(3)N(2), N(3)N(2)N(4), N(2)N(4)N(1), and N(4)N(1)N(3) angles (NBAS) is equal to the sum of the interior angles in a planar tetragon (360.0°)), or almost planar (in [Co**L**] and [Ni**L**] where the NBAS differs from the same sum by no more than 0.2°). It should be noted that, in five complexes, the N(1)M(1)N(2) angle formed by the M atom and the N atoms located at the opposite vertices of this tetragon is exactly 180.0°, and only in the [Co**L**] complex it is slightly smaller (177.6°). An analogous angle in the MN_4 chelate core—N(3)M(1)N(4)—is smaller than 180° in all the complexes and varies from complex to complex, being 162.2° in [Mn**L**], 164.5° in [Fe**L**],

Table 1. Bond lengths, bond angles, and nonbonded angles in complexes [ML]

M	Mn	Fe	Co	Ni	Cu	Zn
Bond lengths in the MN_4 chelate core, pm						
	191.5	189.1	187.5	186.6	190.2	191.1
M(1)–N(2)	186.8	181.9	179.5	180.0	186.9	192.0
M(1)–N(3)	194.4	191.8	189.8	189.2	200.1	208.0
M(1)–N(4)	194.4	191.8	189.0	189.2	200.1	208.0
Selected bond lengths beyond the chelate core, pm						
N(3)–C(3)	142.2	142.4	142.4	142.1	140.7	139.8
C(3)–C(4)	141.7	141.3	141.0	141.0	142.5	143.9
C(4)–N(2)	134.9	135.1	134.8	134.0	133.9	133.9
N(2)–C(5)	134.9	135.1	134.9	134.0	133.9	133.9
C(5)–C(6)	141.7	141.3	141.0	141.0	142.5	143.9
C(6)–N(4)	142.2	142.4	142.4	142.1	140.7	139.8
N(4)–C(7)	132.2	131.5	131.0	130.7	129.9	129.7
C(7)–C(19)	142.6	142.3	142.3	142.2	143.7	145.0
C(19)–C(8)	144.5	143.7	143.4	143.2	144.3	145.0
C(8)–N(1)	138.8	138.7	138.6	138.1	137.9	138.7
N(1)–C(1)	138.8	138.7	138.5	138.1	137.9	138.7
C(1)–C(18)	144.5	143.7	143.4	143.2	144.3	145.0
C(18)–C(2)	142.6	142.3	142.2	142.2	143.7	145.0
C(2)–N(3)	132.2	131.5	131.0	130.7	129.9	129.7
C(3)–C(12)	138.8	138.9	138.9	138.9	139.1	139.3
C(12)–C(13)	140.9	140.9	140.9	140.8	140.5	140.3
C(13)–C(14)	139.0	139.0	139.1	139.2	139.2	139.2
C(14)–C(11)	140.7	140.6	140.5	140.4	140.3	140.2
C(11)–C(4)	140.3	140.3	140.4	140.8	141.0	141.1
C(11)–C(17)	149.0	148.9	148.8	148.7	148.8	148.8
C(17)–C(10)	149.0	148.9	148.8	148.7	148.8	148.8
C(10)–C(5)	140.3	140.3	140.4	140.8	141.0	141.1
C(10)–C(15)	140.7	140.6	140.6	140.4	140.3	140.2
C(15)–C(16)	139.0	139.0	139.0	139.2	139.2	139.2
C(16)–C(9)	140.9	140.9	140.9	140.8	140.5	140.3
C(9)–C(6)	138.8	138.9	138.8	138.9	139.1	139.3
C(19)–C(23)	142.2	141.9	141.7	141.7	141.8	141.8
C(23)–C(24)	137.7	137.8	137.8	137.8	137.8	138.0
C(24)–C(25)	140.4	140.4	140.3	140.4	140.2	139.9
C(25)–C(22)	138.1	138.1	138.2	138.1	138.1	138.3
C(22)–C(8)	141.5	141.7	141.7	141.8	141.9	141.6
C(1)–C(21)	141.5	141.7	141.7	141.8	141.9	141.6
C(21)–C(26)	138.1	138.1	138.2	138.1	138.1	138.3
C(26)–C(27)	140.4	140.4	140.4	140.4	140.2	139.9
C(27)–C(20)	137.7	137.8	137.8	137.8	137.9	138.0
C(20)–C(18)	142.2	141.9	141.7	141.7	141.8	141.8
C(17)–O(1)	123.1	123.1	123.1	123.2	123.2	123.3
Bond angles in the MN_4 chelate core, deg						
N(1)M(1)N(3)	98.9	97.8	97.3	97.4	98.9	100.1
N(3)M(1)N(2)	81.1	82.2	82.7	82.6	81.1	79.9
N(2)M(1)N(4)	81.1	82.2	82.9	82.6	81.1	79.9
N(4)M(1)N(1)	98.9	97.8	97.1	97.4	98.9	100.1
BAS	360.0	360.0	360.0	360.0	360.0	360.0
Nonbonded angles in the N_4 group, deg						
N(1)N(3)N(2)	88.3	87.9	87.8	88.0	86.5	85.2
N(3)N(2)N(4)	101.5	101.3	100.7	100.6	103.5	105.6
N(2)N(4)N(1)	88.3	87.9	88.0	88.0	86.5	85.2
N(4)N(1)N(3)	81.9	82.9	83.3	83.3	83.5	84.0
NBAS	360.0	360.0	359.8	359.9	360.0	360.0

Table 1. (Contd.)

M	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in five-membered chelate ring 1, deg						
M(1)N(3)C(3)	114.3	113.8	113.7	113.8	112.9	112.4
N(3)C(3)C(4)	111.6	111.3	111.0	110.7	112.1	113.1
C(3)C(4)N(2)	113.5	112.9	112.7	112.9	114.7	115.8
C(4)N(2)M(1)	119.1	119.6	119.8	119.5	118.9	118.7
N(2)M(1)N(3)	81.1	82.2	82.7	82.6	81.1	79.9
BAS^{51}	539.6	539.8	539.9	539.5	539.7	539.9
Bond angles in five-membered chelate ring 2, deg						
M(1)N(2)C(5)	119.1	119.6	119.4	119.5	118.9	118.7
N(2)C(5)C(6)	113.5	112.9	112.7	112.9	114.7	115.8
C(5)C(6)N(4)	111.6	111.3	110.9	110.7	112.1	113.1
C(6)N(4)M(1)	114.3	113.8	113.6	113.8	112.9	112.4
N(4)M(1)N(2)	81.1	82.2	82.9	82.6	81.1	79.9
BAS^{52}	539.6	539.8	539.5	539.5	539.7	539.9
Bond angles in six-membered chelate ring 1, deg						
M(1)N(1)C(8)	119.1	120.5	121.1	120.8	119.3	118.8
N(1)C(8)C(19)	122.3	122.3	122.4	122.3	123.1	123.4
C(8)C(19)C(7)	126.7	125.0	124.4	124.1	127.0	129.0
C(19)C(7)N(4)	125.0	123.6	124.1	124.7	125.5	125.3
C(7)N(4)M(1)	121.8	123.7	124.9	124.0	120.6	118.7
N(4)M(1)N(1)	98.9	97.8	97.1	97.4	98.9	100.1
BAS^{61}	713.8	712.9	714.0	713.3	714.4	715.3
Bond angles in six-membered chelate ring 2, deg						
M(1)N(3)C(2)	121.8	123.7	124.6	124.0	120.6	118.7
N(3)C(2)C(18)	125.0	123.6	123.8	124.7	125.5	125.3
C(2)C(18)C(1)	126.7	125.0	124.3	124.1	127.0	129.0
C(18)C(1)N(1)	122.3	122.3	122.3	122.3	123.1	123.4
C(1)N(1)M(1)	119.2	120.5	120.6	120.8	119.3	118.8
N(1)M(1)N(3)	98.9	97.8	97.3	97.4	98.9	100.1
BAS^{62}	713.9	712.9	712.9	713.3	714.4	715.3
Exocyclic bond angles, deg						
C(3)C(12)C(13)	119.1	119.0	118.9	118.8	119.4	120.1
C(12)C(13)C(14)	122.2	122.2	122.2	122.1	121.8	121.5
C(13)C(14)C(11)	120.4	120.4	120.4	120.7	120.7	120.7
C(14)C(11)C(4)	116.3	116.4	116.3	116.0	116.9	117.6
C(14)C(11)C(17)	124.2	124.3	124.4	124.6	123.9	123.2
C(4)C(11)C(17)	119.3	119.3	119.3	119.4	119.3	119.2
C(11)C(17)C(10)	115.0	114.9	114.7	114.4	114.8	115.1
C(17)C(10)C(5)	119.3	119.3	119.3	119.4	119.3	119.2
C(17)C(10)C(15)	124.4	124.3	124.4	124.6	123.9	123.2
C(5)C(10)C(15)	116.3	116.4	116.3	116.0	116.9	117.6
C(10)C(15)C(16)	120.4	120.4	120.4	120.7	120.7	120.7
C(15)C(16)C(9)	122.2	122.2	122.2	122.1	121.8	121.5
C(16)C(9)C(6)	119.1	119.0	118.9	118.8	119.4	120.1
C(9)C(6)C(5)	117.8	117.8	118.0	118.2	118.1	117.8
C(19)C(23)C(24)	122.9	122.4	122.3	122.2	123.0	123.5
C(23)C(24)C(25)	118.7	118.5	118.4	118.4	118.2	118.0
C(24)C(25)C(22)	120.2	120.5	120.6	120.7	120.6	120.3
C(25)C(22)C(8)	122.7	122.4	122.5	122.4	122.9	123.2
C(22)C(8)C(19)	117.0	116.6	116.5	116.5	116.2	116.2
C(8)C(19)C(23)	118.0	118.8	119.2	119.4	118.7	118.0
C(1)C(21)C(26)	122.7	122.4	122.4	122.4	122.9	123.2
C(21)C(26)C(27)	120.2	120.5	120.6	120.7	120.6	120.3
C(26)C(27)C(20)	118.7	118.5	118.4	118.4	118.2	118.0
C(27)C(20)C(18)	122.9	122.4	122.2	122.2	123.0	123.5
C(20)C(18)C(1)	118.0	118.8	119.2	119.4	118.7	118.0
C(18)C(1)C(21)	117.0	116.6	116.4	116.5	116.2	116.2

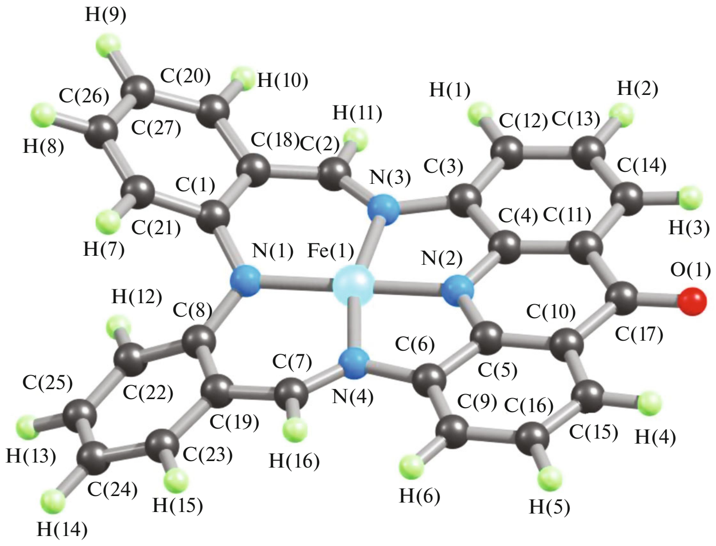


Fig. 1. Molecular structure of [Fe**L**].

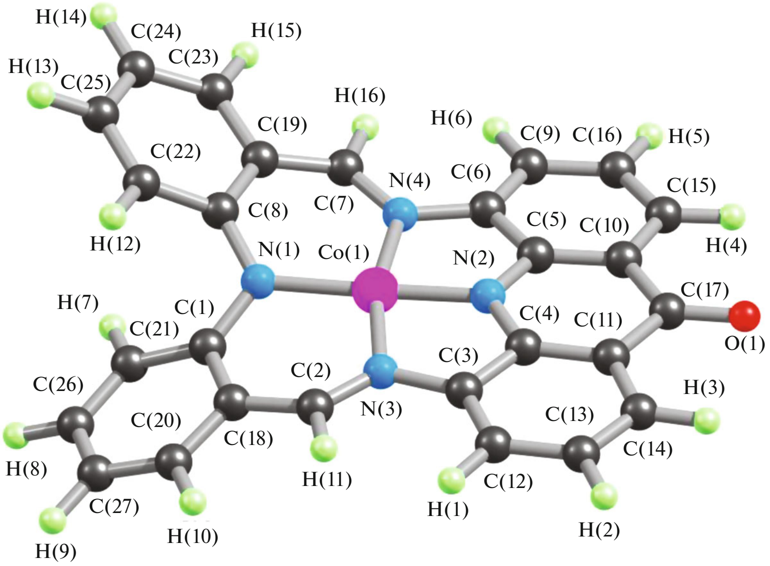


Fig. 2. Molecular structure of [Co**L**].

165.5° in [Co**L**], 165.2° in [Ni**L**], 162.2° in [Cu**L**], and 159.8° in [Zn**L**].

Characterizing the chelate rings, we should note that, in each of the macrocyclic coordination compounds (except [Co**L**]), the five- and six-membered rings are pairwise identical to each other in the set of interior (bond) angles and their sum. This is a remarkable moment, if we take into account that the six-membered chelate rings in the (5665)macrotetracyclic 3*d*-metal complexes, according to [25], differ significantly from each other in both parameters. Both the five- and six-membered chelate rings in these complexes are noncoplanar. However, if the noncoplanarity of the five-membered rings is almost imperceptible (the deviation of the sum of the interior angles in the flat pentagon from 540° does not exceed 0.5°), the noncoplanarity of the six-membered rings is manifested to a significantly greater extent. In all cases, except [Zn**L**], the deviation of the sum of the interior angles in a flat hexagon from 720° is more than 5°. The bond angles outside the chelate rings relatively weakly depend on the nature of the central M(II) ion, which is quite expectable.

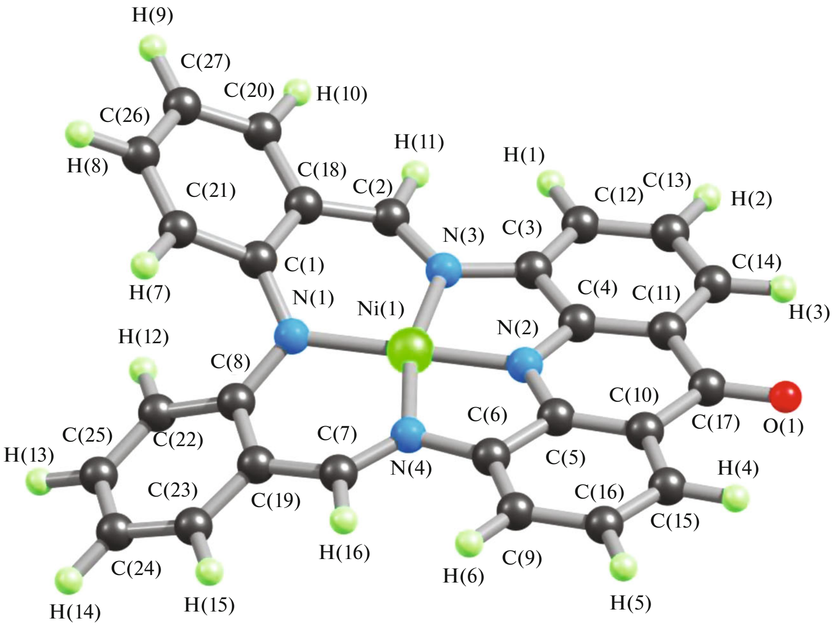


Fig. 3. Molecular structure of [Ni**L**].

CONCLUSIONS

Summing up the discussion of the structural and geometric features of the [M**L**] chelates under consideration, we should note that all of them are asymmetric (Figs. 1–3). Therefore, they are naturally expected to have high electric dipole moment (μ) values. Indeed, the calculated μ for these compounds (6.41 D for [Mn**L**], 6.47 D for [Fe**L**], 6.45 D for [Co**L**], 7.33 D for [Ni**L**], 7.56 for [Cu**L**], and 7.82 D for [Zn**L**]) are consistent with this expectation. In the Mn–Zn series, the μ value remains nearly the same in going from Mn to Co, noticeably increases (by almost 1.0 D) in going from Co to Ni, and continues to increase, but much more weakly, in going from Ni to Zn. The largest electric dipole moment is inherent in the [Zn**L**] chelate. Judging from the parameters of molecular structures, it is precisely [Zn**L**] that has the least pronounced noncoplanarity of both the MN_4 chelate core and all four chelate rings. Nevertheless, each of these complexes is far from coplanarity because two "benzene" rings adjacent to the six-membered chelate rings are not coplanar with them (although the same "benzene" rings adjacent to the five-membered rings are roughly in the same plane with them), which is clearly seen in Figs. 1–3.

The ground states of the (5665)macrotetracyclic Mn(II) and Fe(II) chelates of type [M**L**] are a spin quartet and spin triplet, respectively. Both chelates are complexes with an "intermediate" spin multiplicity. The ground states of the Co(II) and Ni(II) chelates are, respectively, a spin doublet and spin singlet, so that they are low-spin complexes. For the Cu(II) and Zn(II) chelates, in full agreement with theoretical expectations, the ground state is, respectively, a spin doublet and spin triplet. In all complexes, the difference in energy between the ground state and the nearest excited state with a spin multiplicity other than the ground state multiplicity—spin sextet for Mn(II), spin quintet for Fe(II), spin quartet for Co(II), spin triplet for Ni(II), spin quartet for Cu(II), and spin triplet for Zn(II)—is rather large being 35.8, 68.4, 93.6, 101.1, 130.3, and 130.1 kJ/mol, respectively. Hence, the possibility of the manifestation of spin isomerism (spin crossover) should be excluded.

The calculated standard thermodynamic parameters of formation of macrocyclic metal chelates [M**L**] ($\Delta H^0_{f,298}$, $S^0_{f,298}$, and $\Delta G^0_{f,298}$) are presented in Table 2. As is seen, the $\Delta H^0_{f,298}$ and $\Delta G^0_{f,298}$ values for all metal chelates are positive, which indicates the impossibility

Table 2. Standard enthalpies $\Delta H^0_{f,298}$, entropies $S^0_{f,298}$ and Gibbs energies $\Delta G^0_{f,298}$ of formation for M(II) chelates [M**L**]

M	$\Delta H^0_{f,298}$, kJ/mol	$S^0_{f,298}$, J/(mol K)	$\Delta G^0_{f,298}$, kJ/mol
Mn	–34.6	956.9	144.6
Fe	89.1	951.6	268.5
Co	117.2	949.5	298.0
Ni	124.6	949.3	305.4
Cu	289.1	957.2	468.6
Zn	160.9	963.6	341.0

of the formation of these complexes from elementary substances. It should also be noted Very high values of the standard entropy of formation ($S^0_{f,298}$) for all these metal complexes should be noted. The [Ni**L**] complex is not distinguished by $S^0_{f,298}$ thermodynamic characteristics from the other M(II) chelates of this type. Since it was synthesized under common conditions of complexation, there are very good reasons to believe that the other M(II) can also be obtained in the experiment. It is worth noting that the $\Delta H^0_{f,298}$ and $\Delta G^0_{f,298}$ values for the [Mn**L**] chelate are much lower than those for the other metal chelates.

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