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THEORETICAL INORGANIC CHEMISTRY

Quantum-Chemical Calculation of Molecular Structures of (5656)Macrotetracyclic 3*d* Metal Complexes "Self-Assembled" in Quaternary Systems M(II) Ion–Ethanedithioamide–Formaldehyde–Ammonia by the Density Functional Theory Method

D. V. Chachkov and O. V. Mikhailov
Joint Supercomputer Center, Kazan Branch, Russian Academy of Sciences,
ul. Lobachevskogo 2/31, Kazan, Tatarstan, 420111 Russia
Kazan National Research Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia

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Abstract—The geometric parameters of (5656)macrotetracyclic complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with the NNNN-coordination of donor sites of the chelant formed by the template reactions in the M(II)–ethanedithioamide–formaldehyde–ammonia systems have been calculated by the OPBE/TZVP hybrid density functional theory (DFT) method with the use of the Gaussian09 program package. In all complexes, five-membered chelate rings (almost identical to each other in each complex) are nonplanar. For all M(II) ions under consideration, two additional six-membered nonplanar chelate rings formed as a result of template "cross-link" are turned at considerable angles with respect to the five-membered rings. The six-membered rings are located on different sides of the NNNN plane of the nitrogen donor atoms.

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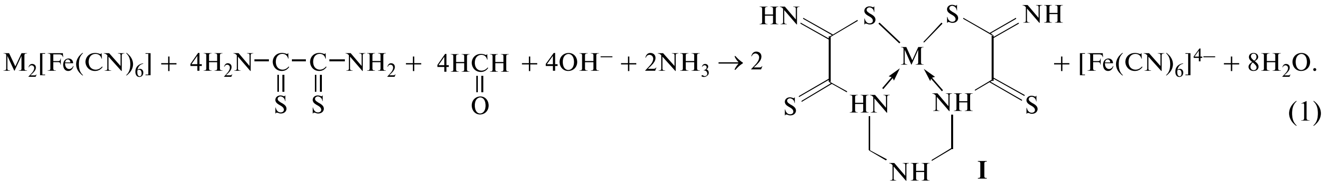
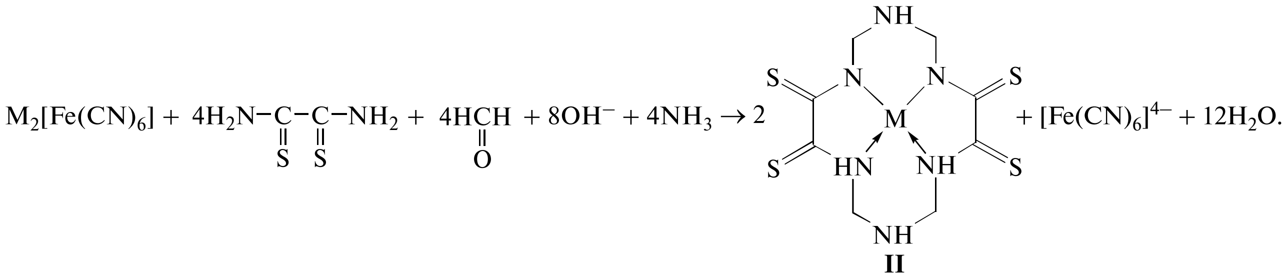
Previously [1], it has been experimentally demonstrated that "self-assembly" occurs in quaternary systems M(II)–ethanedithioamide ($H_2N-C(=S)-C(=S)-NH_2$)—formaldehyde–ammonia (M = Ni, Cu) in metal(II) hexacyanoferrate(II) gelatin-immobilized matrices (GIM). It has been shown by EPR and magnetic susceptibility measurements that the template reaction leads to formation of (565)macrotricyclic complexes of type **I** by the following scheme:



(1)

DFT quantum-chemical calculation of the complexes formed in these systems [2] revealed the details of coordination of the forming macrocyclic ligand to 3*d*-metal ions, in particular, to Ni(II) and Cu(II). In these systems, "self-assembly" of more complicated (5656)macrotetracyclic metal chelates of type **II** is possible by the following overall scheme [3]:



(2)

II

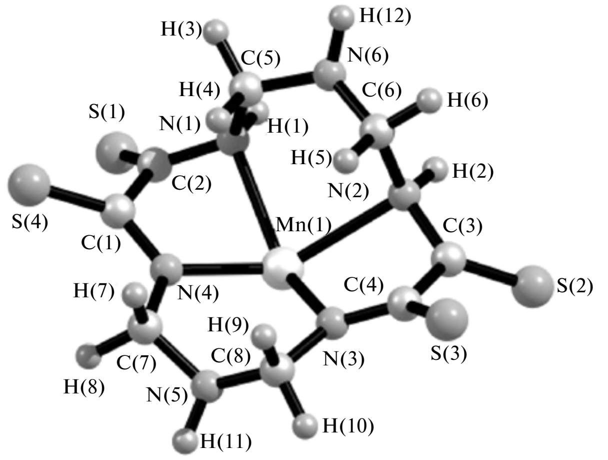


Fig. 1. Molecular structure of the Mn(II) complex of type **II**.

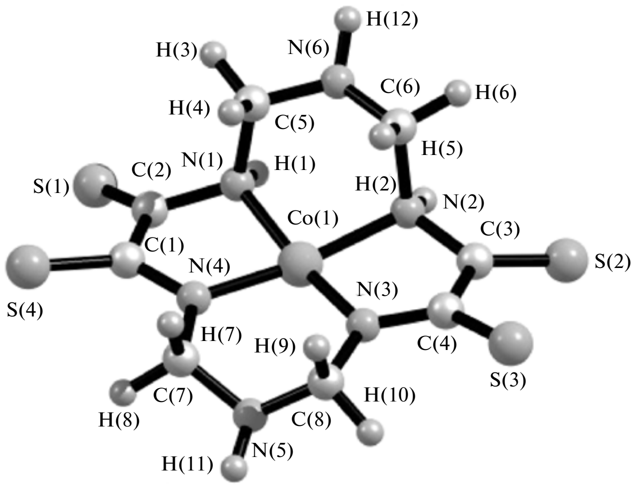


Fig. 2. Molecular structure of the Co(II) complex of type **II**.

it seems to be of interest to perform DFT quantum-chemical calculation of the molecular structures of these complexes.

COMPUTATIONAL DETAILS

Quantum-chemical calculations were performed by the density functional theory (DFT) method using the standard TZVP extended spit-valence basis set [4,
1 5] and the OPBE nonhybrid functional [6, 7]. In the case of 3*d* metal complexes, this level of theory has been shown to give sufficiently accurate relative energy stabilities [7–11]. At the same time, the OPBE/TZVP method reliably characterizes the geometric parameters of molecular structures. Calculations were performed with the Gaussian09 program package [12]. The correspondence of the found stationary points to energy minima was proved in all cases by the calculation of the second derivatives of energy with respect to the atom coordinates: all equilibrium structures corresponding to minima of the potential energy surfaces had only real positive frequency values. Quantum-chemical calculations were carried out at the Joint
2 Supercomputer Center, Kazan Branch, Russian Academy of Sciences (http://kbjscc.knc.ru).

RESULTS AND DISCUSSION

In complete correspondence with theoretical expectations, the group of the four nitrogen atoms that form the MN_4 chelate core is ideally planar in all complexes of type **II** under consideration (the sum of the (N1N2N3), (N2N3N4), (N3N4N1), and (N4N1N2) angles is 360.0°). Nevertheless, the MN_4 chelate core itself is planar in none of the complexes; moreover, in the Mn(II) and Zn(II) complexes, the deviation of this core from coplanarity is rather significant (the sum of the (N1M1N2), (N2M1N3), (N3M1N4), and (N4M1N1) bond angles (BAS) is 336.7° for Mn(II), 354.9° for Fe(II) and Cu(II), 358.5° for Co(II) and Ni(II), and 348.4° for Zn(II)). In each of the complexes, the lengths of two of the four M–N bond are the same; as for the distances between neighboring nitrogen atoms in chelate rings and the (NMN) bond angles, two of them are the same, while the other two are different (Table 1). Comparison of these data to the M–N bond lengths in similar M(II) complexes with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecane-4,5,11,12-tetrathione [13] (in these complexes, the six-membered rings contain an O atom rather than an NH group) shows that these bonds are on the whole longer in the Mn(II), Ni(II), Cu(II), and Zn(II) complexes, shorter in the Fe(II) complex, and nearly the same in the Co(II) complex.

Two additional six-membered chelate rings formed upon the template cross-link and containing an N–C–N–C–N group do not lie in the same plane with the (NNNN) plane of the donor atoms even in the case of Co(II) and Ni(II) complexes with a structure relatively close to planar. The deviation for each ring in each complex is different (Figs. 1–3, Table 1). The bond angle sums BAS^{61} and BAS^{62} differ significantly from the sum of the interior angles in a planar hexagon (720°). These sums depend only slightly on the nature of the 3*d* metal, but differ rather strongly in the same complex (626.7° and 667.1° in the Mn(II) complex, 627.9° and 678.0° for Fe(II), 632.7° and 677.6° for Co(II), 632.2° and 678.4° for Ni(II), 627.3° and 675.7° for Cu(II), and 624.0° and 672 for Zn(II)) (Table 1). An analogous phenomenon has been reported in [13]. The torsion angles are rather large (Table 1), which is one more evidence of the considerable ring distortion (despite this fact, each of the rings has two pairs of identical angles).

Both five-membered rings in the metal chelates under consideration are also nonplanar (the BAS^{51} and BAS^{52} in them are smaller than the sum of the interior angles of a planar pentagon (540°)); however,

Table 1. Selected parameters of the molecular structures of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes **II**

	Mn	Fe	Co	Ni	Cu	Zn
M–N bond lengths, pm						
M1N1	243.3	201.2	197.1	194.2	212.2	229.6
M1N2	243.3	201.2	197.1	194.2	212.2	229.6
M1N3	200.9	187.1	186.9	195.8	194.7	194.3
M1N4	200.9	187.1	186.9	195.8	194.7	194.3
Selected bond lengths out of the chelate core, pm						
N1C5	149.2	150.1	149.9	150.0	149.8	149.5
C5N6	143.3	143.6	143.3	143.4	143.2	143.2
N6C6	143.3	143.6	143.3	143.4	143.2	143.2
C6N2	149.2	150.1	149.9	150.0	149.8	149.5
N2C3	141.5	145.0	146.4	146.0	142.9	142.5
C3C4	150.4	148.0	147.4	147.3	149.3	150.2
C4N3	133.4	135.4	134.7	134.4	133.0	133.3
N3C8	145.4	145.0	144.7	144.8	145.0	145.5
C8N5	144.9	143.8	143.9	143.7	144.1	144.5
N5C7	144.9	143.8	143.9	143.7	144.1	144.5
C7N4	145.4	145.0	144.7	144.8	145.0	145.5
N4C1	133.4	135.4	134.7	134.4	133.0	133.3
C1C2	150.4	148.0	147.4	147.3	149.3	150.2
C2N1	141.5	145.0	146.4	146.0	142.9	142.5
C1S4	167.0	167.0	167.6	167.5	167.9	167.1
C2S1	163.9	163.5	163.1	163.0	163.5	163.5
C3S2	163.9	163.5	163.1	163.0	163.5	163.5
C4S3	167.0	167.0	167.6	167.5	167.9	167.1
N5H11	101.0	101.2	101.3	101.3	101.1	101.0
NMN bond angles, deg						
N1M1N2	83.5	91.2	93.1	92.4	92.4	85.7
N2M1N3	75.3	82.9	83.2	83.7	81.3	78.9
N3M1N4	102.6	97.9	99.0	98.7	99.9	104.9
N4M1N1	75.3	82.9	83.2	83.7	81.3	78.9
BAS	**336.7**	**354.9**	**358.5**	**358.5**	**354.9**	**348.4**
Interior (non-bonded) NNN angles, deg						
N1N2N3	88.9	89.4	89.8	90.2	89.1	89.6
N2N3N4	91.1	90.6	90.2	89.8	90.9	90.4
N3N4N1	91.1	90.6	90.2	89.8	90.9	90.4
N4N1N2	88.9	89.4	89.8	90.2	89.1	89.6
NBAS	**360.0**	**360.0**	**360.0**	**360.0**	**360.0**	**360.0**
Bond angles in five-membered ring 1, deg						
M1N1C2	96.6	106.1	109.4	109.4	104.8	99.3
N1C2C1	112.7	111.3	111.2	110.9	112.5	112.8
C2C1N4	109.3	110.8	110.7	110.6	111.2	110.1
C1N4M1	121.8	118.4	119.3	118.8	117.9	120.3
N4M1N1	75.3	82.9	83.2	83.7	81.3	78.9
BAS^{51}	**515.7**	**529.5**	**533.8**	**533.4**	**527.7**	**521.4**
Bond angles in five-membered ring 2, deg						
M1N2C3	96.6	106.1	109.4	109.4	104.8	99.3
N2C3C4	112.7	111.3	111.2	110.9	112.5	112.8
C3C4N3	109.3	110.8	110.7	110.6	111.2	110.1
C4N3M1	121.8	118.4	119.3	118.8	117.9	120.3
N3M1N2	75.3	82.9	83.2	83.7	81.3	78.9
BAS^{52}	**515.7**	**529.5**	**533.8**	**533.4**	**527.7**	**521.4**

Table 1. (Contd.)

	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in six-membered ring 1, deg						
M1N1C5	102.2	101.5	102.7	103.4	98.9	100.5
N1C5N6	109.9	107.7	107.9	107.4	108.9	109.2
C5N6C6	119.0	118.3	118.4	118.2	119.3	118.9
N6C6N2	109.9	107.7	107.9	107.9	108.9	109.2
C6N2M1	102.2	101.5	102.7	103.4	98.9	100.5
N2M1N1	83.5	91.2	93.1	92.4	92.4	85.7
BAS^{61}	**626.7**	**627.9**	**632.7**	**632.2**	**627.3**	**624.0**
Bond angles in six-membered ring 2, deg						
M1N4C7	114.4	133.2	122.2	122.7	119.7	115.4
N4C7N5	108.5	109.2	109.6	109.8	109.7	109.1
C7N5C8	118.7	115.3	115.0	114.7	117.0	118.7
N5C8N3	108.5	109.2	109.6	109.7	109.7	109.1
C8N3M1	114.4	123.2	122.2	122.7	119.7	115.4
N3M1N4	102.6	97.9	99.0	98.7	99.9	104.9
BAS^{62}	**667.1**	**678.0**	**677.6**	**678.4**	**675.7**	**672.6**
Exocyclic bond angles, deg						
C5N1C2	118.7	116.5	114.3	114.4	116.9	117.8
N1C2S1	121.1	119.7	119.3	119.5	120.4	120.7
S1C2C1	125.7	128.9	129.3	129.5	126.8	126.1
C2C1S4	120.7	122.0	122.1	122.2	121.3	120.7
S4C1N4	129.9	127.2	127.2	127.2	127.4	129.3
C1N4C7	121.9	118.4	118.1	118.2	120.8	121.9
C8N3C4	121.9	118.4	118.1	118.2	120.8	121.9
S3C4C3	129.9	127.2	127.2	127.2	127.4	129.3
C4C3S2	125.7	128.9	129.3	129.5	126.8	126.1
S2C3N2	121.1	119.7	119.3	119.5	120.4	120.7
C3N2C6	118.7	116.5	114.3	114.4	116.9	117.8
Selected torsion angles, deg						
N2N1C5N6	31.6	30.0	29.8	29.6	30.5	31.1
N1N2C6N6	−31.6	−30.0	−29.8	−29.6	−30.5	−31.1
N4N3C8N5	31.3	31.2	31.5	31.4	31.2	30.9
N3N4C7N5	−31.3	−31.2	−31.5	−31.4	−31.2	−30.9
N2M1N1C5	−56.7	−65.9	−64.1	−65.2	−69.1	−61.6
N1M1N2C6	56.7	65.9	64.1	65.2	69.1	61.6
N4M1N3C8	17.6	5.0	2.1	1.3	2.2	8.0
N3M1N4C7	−17.6	−5.0	−2.1	−1.3	−2.2	−8.0
N1M1N3C8	99.7	96.5	104.8	106.0	94.4	102.6
N2M1N4C7	−99.7	−96.5	−104.8	−106.0	−94.4	−102.6
S1C2N1M1	−122.3	−141.2	−150.8	−150.1	−139.2	−130.0
S2C3N2M1	122.3	141.2	150.8	150.1	139.2	130.0
S3C4N3M1	159.5	172.2	167.0	167.6	162.6	158.8
S4C1N4M1	−159.5	−172.2	−167.0	−167.6	−162.6	−158.8
N1C2C1N4	−52.0	−29.1	−25.6	−26.0	−37.3	−46.3
N2C3C4N3	52.0	29.1	25.6	26.0	37.3	46.3
S1C2C1S4	−61.1	−33.4	−28.8	−28.7	−42.0	−54.1
S2C3C4S3	61.1	33.4	28.8	28.7	42.0	54.1

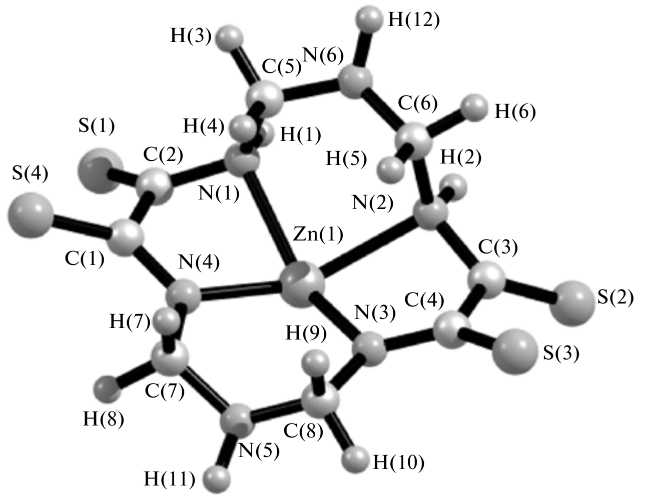


Fig. 3. Molecular structure of the Zn(II) complex of type **II**.

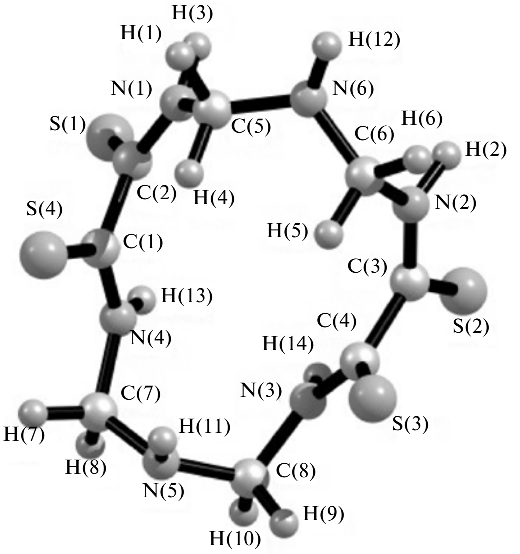


Fig. 4. Molecular structure of the chelant involved in complexes **II**.

as distinct from the six-membered rings, the five-membered rings are almost identical (Table 1). All angles in these rings are different. In all complexes **II**, the N5 and N6 atoms not bonded to the M atoms are located on different sides of the plane formed by the N1, N2, N3, and N4 donor atoms.

The ground state of macrotetracyclic Mn(II) chelate **II** is a spin sextet. It is a high-spin complex, whereas analogous Co(II) and Ni(II) chelates are low-spin complexes with the doublet and singlet ground state, respectively. As expected, the ground state of the Cu(II) and Zn(II) chelates is respectively, a spin doublet and a spin singlet. The ground state of the Fe(II) chelate is a spin triplet; the difference in energy between the ground state and the nearest excited state (a spin quintet) is only 12.7 kJ/mol. It is worth noting that the ground state of the Fe(II) chelate with 1,8-dioxa-3,6,10,13-tetraazacyclotetradecane-4,5,11,12-tetrathione is a spin quintet, the difference in energy between this state and the nearest triplet being 58.8 kJ/mol [13].

Complexes **II** under consideration have rather high electric dipole moments: 3.51 (Mn(II)), 5.66 (Fe(II)), 5.91 (Co(II)), 5.82 (Ni(II)), 5.32 (Cu(II)), and 4.36 D (Zn(II)). As can be seen, these dipole moments increase in going from Mn to Ni and decrease in going from Ni to Zn. On the whole, high electric dipole moments for these complexes are quite natural since they are asymmetric. For the complexes considered in [13], the electric dipole moments are even higher (5,53, 5,73, 6,44, 6,52, 6,31, and 5.57 D, respectively).

Table 2. Standard thermodynamic parameters of formation of M(II) complexes **II**

M(II)	$\Delta H^0_{f,\,298}$, kJ/mol	$S^0_{f,\,298}$, J/(mol K)	$\Delta G^0_{f,\,298}$, kJ/mol
Mn(II)	398.9	747.5	412.8
Fe(II)	562.8	716.9	584.4
Co(II)	599.0	711.8	623.0
Ni(II)	593.3	708.1	618.3
Cu(II)	716.4	721.5	738.4
Zn(II)	586.8	729.0	609.1

Table 2 summarizes the standard thermodynamic parameters of formation of complexes **II** obtained by quantum-chemical calculation. It can be seen that the $\Delta H^0_{f,298}$ and $\Delta G^0_{f,298}$ values for all complexes are positive and rather significant, which points to the impossibility of formation of these complexes from individual elements. In this context, it can be suggested that overall process (2) is most likely thermodynamically forbidden in solution or solid phase, but can be realized in organizing systems based on metal complex gelatin-immobilized matrix implants [3].

Thus, the (5656)macrotetracyclic chelates **II** are nonplanar; despite this fact, the groups of the four donor nitrogen atoms (NNNN) in them are roughly coplanar. The complexes have a pyramidal structure in which the M atom is only slightly above the NNNN plane. At the same time, the trend in the change in M—N bond lengths in the Mn—Zn series is on the whole coincident with the change in the radii of doubly charged ions in this series. All complexes are sharply asymmetric and, at best, have one symmetry element (namely, a symmetry plane passing through the M atom and two nitrogen atoms, N5 and N6, of the six-membered chelate rings).

The calculation of the molecular structure of the chelant (Fig. 4) involved in the complexes has shown that it is nonplanar (which is quite expected). The

14-membered macrocyclic ring in both the ligand itself and in all metal chelates under consideration is convex: the sum of the interior angles is smaller than the sum of the interior angles of a planar tetradecagon (2160°): by 72.4° in the chelant, 82.7° in the Mn(II) complex, 78.2° for Fe(II), 72.6° for Co(II), 75.0° for Ni(II), 74.4° for Cu(II), and 79.4° for Zn(II)). As can be seen, the deviation from 2160° in the complexes is always larger than in the chelant; thus, it can be stated that the complexation of 3*d* M(II) ions with this chelant is accompanied by an increase in the degree of distortion of its structures, although not too significant.

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Translated by G. Kirakosyan

SPELL: 1. nonhybrid, 2. Kazan