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Possibility of Template Synthesis with Junction of Metallacycles Containing *trans*-Located Nitrogen Atoms in the 3*d* Metal(II) Ion–Dithiooxamide–Acetone Systems As Predicted by DFT Simulation Data

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Abstract—Simulation of thermodynamic and geometry parameters of Mn(II), Ni(II), and Zn(II) complexes with macrocyclic ligands has been performed using non-hybrid DFT method OPBE/TZVP implemented in GAUSSIAN'09 software. Such complexes with NNSS coordination of the donor centers and *trans* orientation of nitrogen and sulfur atoms can be formed via template processes in the M(II)–dithiooxamide–acetone systems.

Keywords: template synthesis, macrocyclic chelate, dithiooxamide, acetone, molecular structure, quantum-chemical simulation, DFT

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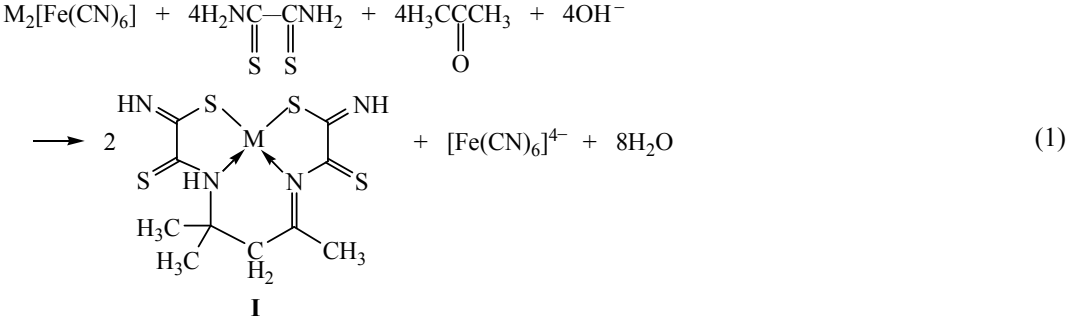
Earlier we have experimentally observed template synthesis in the tertiary systems of M(II)–dithiooxamide (ethanedithioamide)–acetone (M = Co, Ni, or Cu) proceeding in metal hexacyanoferrate(II) gelatin-immobilized template implants [1–3] [scheme (1)].

Furthermore, we have elucidated details of coordination of the so formed ligand (chelant) with the corresponding metal ion. The first stage of the process consists in the formation of bis-chelate coordination compounds of Co(II), Ni(II), or Cu(II) (type **I** complexes) containing two singly deprotonated molecules of dithiooxamide with *cis* orientation of N and S donor centers in the inner sphere. In the second stage the two metal chelate cycles were linked via acetone molecules to form a closed loop. Quantum-chemical DFT simulation of molecular structures of the formed (565)macrotricyclic metal chelate has been performed for the cases of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) [4, 5]. In particular, it has been demonstrated that none of the formed metal chelates was planar, contrary to expectations. Moreover, the MN_2S_2 chelate node in these complexes was not planar as well. However, a different scheme of the template synthesis is possible, resulting in the formation of type **II** complexes with *trans*-located N



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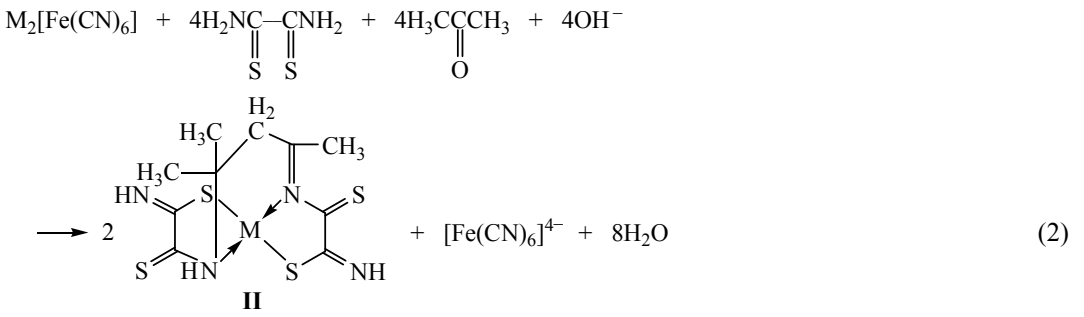

(2)

and S donor atoms of the ligands in the chelate node, linked via the carbonyl-containing component (acetone) [scheme (2)].

Such complexes have not been experimentally observed so far [6]. In view of that, quantum-chemical simulation of the type **II** complexes with *trans* location of the chelant donor centers with respect to M(II) ion is of special interest.

According to our DFT OPBE/TZVP simulation, type **II** complexes could only exist in the cases of Mn(II), Ni(II), and Zn(II). Unlike that, in the cases of Fe(II), Co(II), and Cu(II) the geometry optimization at any multiplicity led to physically meaningless structures. The mentioned simulations considered the gas phase; however, due to the special features of the formed ligand and the studied metal ions the result will be the same in the case of the condensed phase, at least qualitatively. Indeed, the conclusion was confirmed by PCM quantum-chemical simulation of the type **II** (565)macrotricyclic complexes in the condensed phase [7]. At the same time, PCM simulation did not involve any geometry optimization, and the corresponding results were seemingly less reliable than those obtained using the DFT OPBE/TZVP method for the gas phase. The simulation results (bond lengths, bond angles, and non-bond angles in the group of donor atoms of the MN_2S_2 chelate node) are collected in Table 1.

Molecular structures of the considered type **II** complexes of Mn(II), Ni(II), and Zn(II) are shown in Figs. 1–3. As seen from the figures, the (565)macrotricyclic chelates contained no symmetry elements. As the studied complexes had no center of symmetry, the high dipole moments were anticipated. Indeed, the OPBE/TZVP simulation gave the μ values of 7.19 [Mn(II)], 7.32 [Ni(II)], and 7.33 [Zn(II)] D. The close values of the dipole moment for the studied molecules was due to the bulky structure of the ligand in the inner sphere of the complexes, not easily accessible for coordination bonding with M(II) ions: in such a case the complex asymmetry and the related dipole moment value were mainly governed by the ligand structure.

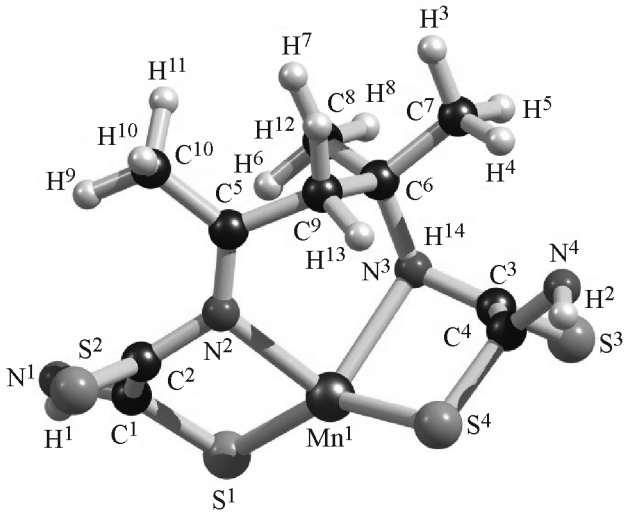

Fig. 1. Molecular structure of type **II** complex of Mn(II).

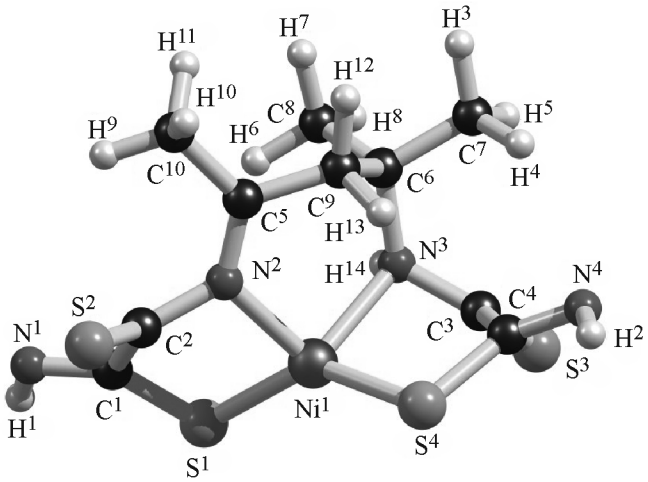

Fig. 2. Molecular structure of type **II** complex of Ni(II).

Table 1. Bond lengths, bond angles, and torsion angles in the M(II) complexes of type **II**

M	Mn	Ni	Zn	M	Mn	Ni	Zn
Bond lengths in the MN_2S_2 chelate node, pm							
$M^1–N^2$	215.9	196.0	211.8	$M^1–S^1$	234.0	219.6	225.6
$M^1–N^3$	234.0	209.6	232.3	$M^1–S^4$	235.0	222.3	226.1
Selected bond lengths out of the chelate node, pm							
$N^2–C^5$	129.1	129.3	129.0	$C^2–N^2$	140.0	140.2	139.6
$C^5–C^9$	150.6	150.4	150.5	$C^1–N^1$	127.6	127.6	127.7
$C^9–C^6$	155.7	155.0	155.8	$C^2–S^2$	163.6	163.7	163.6
$C^6–N^3$	151.5	151.7	151.4	$C^4–N^4$	127.6	127.7	127.6
$N^3–C^3$	141.7	142.5	141.4	$C^3–S^3$	164.2	164.0	163.9
$C^3–C^4$	150.3	150.0	150.3	$C^5–C^{10}$	149.3	149.3	149.3
$C^4–S^4$	177.4	176.7	177.6	$C^6–C^8$	153.2	153.2	153.2
$S^1–C^1$	177.9	177.5	178.0	$C^6–C^7$	153.2	153.2	153.2
$C^1–C^2$	150.9	150.6	151.2				
Bond angles in the MN_2S_2 chelate node, deg							
$S^1M^1N^2$	85.5	89.4	88.7	$N^3M^1S^1$	118.5	119.5	116.9
$N^2M^1S^4$	113.2	112.6	115.8	Sum of the bond angles (BAS)	405.3	412.7	411.2
$S^4M^1N^3$	88.1	91.2	89.8				
Internal angles in the N_2S_2 node, deg							
$N^3S^1N^2$	51.6	53.3	52.6	$S^4N^3S^1$	75.7	74.8	73.4
$S^1N^2S^4$	82.1	80.3	78.1	Sum of the internal angles NBAS	263.0	263.5	258.0
$N^2S^4N^3$	53.6	55.1	53.9				
Bond angles in the five-membered chelate cycle 1, deg							
$M^1N^3C^3$	93.4	97.4	93.9	$C^4S^4M^1$	95.0	96.0	95.4
$N^3C^3C^4$	117.2	116.2	116.7	$S^4M^1N^3$	88.1	91.2	89.8
$C^3C^4S^4$	110.2	108.5	110.9	Sum of the angles VAS[51]	503.9	509.3	506.7
Bond angles in the five-membered chelate cycle 2, deg							
$M^1N^2C^2$	107.1	108.6	106.4	$C^1S^1M^1$	96.7	96.7	95.6
$N^2C^2C^1$	112.2	112.0	112.4	$S^1M^1N^2$	85.5	89.4	88.7
$C^2C^1S^1$	113.9	112.2	115.5	Sum of the angles VAS[52]	515.4	518.9	518.6
Bond angles in the extra six-membered chelate cycle, deg							
$M^1N^3C^6$	116.3	115.6	115.7	$C^5N^2M^1$	124.9	123.5	124.8
$N^3C^6C^9$	111.3	110.9	111.3	$N^2M^1N^3$	90.6	97.8	91.2
$C^6C^9C^5$	116.5	116.8	116.1	Sum of the angles VAS[6]	677.4	682.1	676.6
$C^9C^5N^2$	117.8	117.5	117.5				

Table 1. (Contd.)

M	Mn	Ni	Zn	M	Mn	Ni	Zn
Bond angles out of the chelate cycles, deg							
$C^{10}C^5N^2$	123.9	124.3	124.1	$C^7C^6N^3$	110.5	110.8	110.6
$C^5N^2C^2$	127.6	128.0	128.3	$C^6N^3C^3$	123.1	122.4	122.3
$N^2C^2S^2$	123.3	123.7	123.6	$N^3C^3S^3$	120.6	120.5	121.2
$S^2C^2C^1$	124.0	123.8	123.6	$S^3C^3C^4$	121.6	122.8	121.5
$C^2C^1N^1$	118.0	119.1	117.2	$C^3C^4N^4$	120.8	121.3	120.6
$N^1C^1S^1$	128.1	128.7	127.2	$N^4C^4S^4$	128.9	130.1	128.4
$C^8C^6N^3$	105.2	105.5	105.4	$C^7C^6C^8$	109.3	109.5	109.3
Torsion angles, deg							
$M^1N^2C^5C^9$	–10.3	–6.3	–9.9	$M^1S^4C^4C^3$	–27.9	–21.5	–28.0
$M^1N^3C^6C^9$	24.6	24.4	22.7	$N^2C^2C^1S^1$	52.0	43.0	47.7
$N^2C^5C^9C^6$	69.6	62.3	70.0	$N^3C^3C^4S^4$	71.0	60.0	68.1
$N^3C^5C^9C^5$	–75.2	–70.3	–74.4	$S^3C^3C^4N^4$	76.0	64.6	72.7
$C^6N^3M^1S^1$	98.5	108.0	104.9	$S^2C^2C^1N^1$	58.1	48.9	53.2
$C^5N^2M^1S^4$	65.0	68.6	65.6	$C^5N^2C^3C^1$	119.1	128.4	122.4
$M^1N^2C^2C^1$	–54.1	–51.6	–50.0	$C^6N^3C^3C^4$	61.9	66.6	64.7
$M^1N^3C^3C^4$	–62.7	–60.0	–59.2	$S^1N^2S^4N^3$	83.3	80.3	82.8
$M^1S^1C^1S^2$	–20.5	–13.6	–17.7				

In each of the studied Mn(II), Ni(II), and Zn(II) coordination compounds the M–N and M–S bond lengths were different, the M–S bonds being on the average longer than the M–N bonds, due to the larger radius of sulfur atom as compared with nitrogen one. However, in the case of the Mn(II) chelate the M^1–N^3 bond length was almost equal to that of the M^1–S^1 bond, whereas in the case of the Zn(II) complex the respective M–N bond was even longer than both M–S bonds (Table 1). As the ionic radii of the considered M(II) followed the $r_{Ni(II)} < r_{Zn(II)} < r_{Mn(II)}$ series, the M–S and M–N bond lengths were in general the shortest in the Ni(II) chelate and the longest in the Mn(II) chelate. All studied metal chelates possessed pseudo tetrahedral coordination of the ligand donor centers at M(II) ion, the deviation from coplanarity being fairly significant: sum of the bond angles in the MN_2S_2 chelate node was 405.3°, 412.7°, and 411.2° for the complexes of Mn(II), Ni(II), and Zn(II), respectively. The found coordina-tion type was not surprising, as tetrahedral geometry or close to it has been recognized as prevailing for Zn(II) ion with coordination number of 4; such geometry is typical of Mn(II) as well. As far as Ni(II) complexes are concerned, square planar or quasi-rhombic coordination of donor ligands is the most typical at coordination number of 4. However,

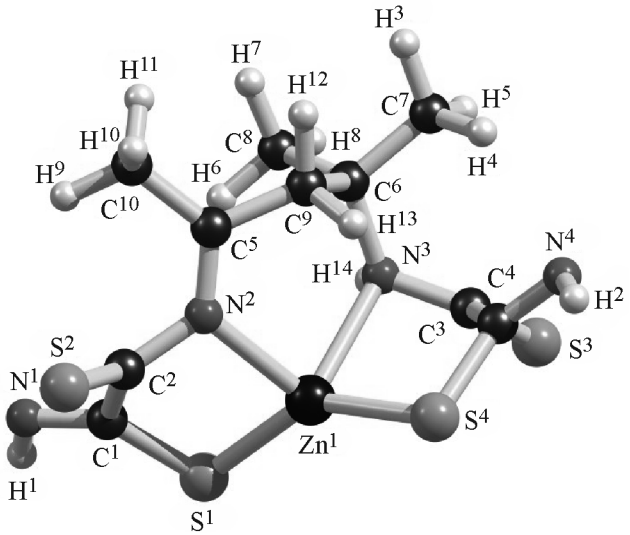

Fig. 3. Molecular structure of type **II** complex of Zn(II).

Table 2. Standard enthalpy, entropy, and Gibbs energy of type **II** chelates formation with various M(II) ions

M	$\Delta H^0_{f,298}$, kJ/mol	$S^0_{f,298}$, J mol^{-1} K^{-1}	$\Delta G^0_{f,298}$, kJ/mol
Mn	190.9	798.8	171.6
Ni	456.1	797.7	436.6
Zn	354.0	778.8	343.7

quasi-tetrahedral coordination of the donor atoms at the central ion has been found in Ni(II) complexes with bulky ligands in the inner coordination sphere [8].

Nonetheless, we failed to unambiguously explain the fact that type **II** complexes could be formed by Mn(II), Ni(II), and Zn(II) but were unstable in the cases of Fe(II), Co(II), and Cu(II). Tetrahedral coordination is not typical of Fe(II) complexes [8] but such reasoning cannot be operative for Cu(II) and especially for Co(II). No simple correlation was revealed between the ability of M(II) ions to form type **II** complexes and their electronic configuration; however, two of the three ions capable of such complex formation had either fully filled $3d^{10}$ orbital [Mn(II)] or the half-filled $3d^5$ one [Zn(II)]. Similarly, no correlation was found between the discussed complex formation ability and the Pearson "hardness" of M(II) ions quantitatively reflected in the orbital electronegativity [9].

Noteworthily, the sum of non-bond (internal) angles in the N_2S_2 donor atom group was much below 360° (258.0°–263.5°, Table 1), evidencing the non-coplanarity of the fragment. The Zn(II) complex had the most prominent non-coplanarity. The simulation confirmed that the five-membered chelate metallacycles containing sulfur and nitrogen donor atoms were not identical. None of the complexes contained a pair of equal bond angles (Table 1), and their sums differed by at least 10°. None of those cycles was planar or close to planar; the corresponding sums of bond (internal) angles differed from that in the planar pentagon by at least 20°. The higher deviation from coplanarity was found for cycles containing the N^3 imine nitrogen. The six-membered cycles containing two donor nitrogen atoms each deviated from coplanarity even more, the corresponding sums of bond angles differing from that in the planar hexagon by at least 40° (Table 1). Furthermore, none of the bond angles out of the chelate cycles in any of the studied complexes were equal; similar was true for the bond lengths both in the chelate cycles and out of them. Those geometry parameters were relatively independent of the M(II) nature, as the latter was located quite far; for instance, the C^5–C^{10}, C^6–C^8, and C^6–C^7 were equal in length (Table 1). Interestingly, lengths of the peripheral N–H bonds (N^1–H^1 and N^4–H^2) in all studied complexes equaled 102.4 pm; the N–H bonds at the donor N^3 atoms were slightly shorter: 102.0 pm in the Mn(II) and Ni(II) complexes and 101.9 pm in the Zn(II) complex. On the contrary, the central ion nature influenced more on the torsion angles values; those geometry parameters were different in the studied type **II** complexes (Table 1).

The ground state, the nearest excited state, and their energy difference in the studied complexes were as follows: spin sextet and quartet (82.3 kJ/mol) for Mn(II); spin triplet and singlet (11.5 kJ/mol) for Ni(II); and spin singlet and triplet (82.2 kJ/mol) for Zn(II). The Ni(II) and Mn(II) complexes thus were high-spin ones. Noteworthily, the triplet ground state is typical of Ni(II) complexes [8]; however, the low energy difference showed that the crossover phenomenon was possible for type **II** Ni(II) complex.

Table 2 shows standard thermodynamic functions of formation of the studied type **II** complexes. In all the cases those parameters were positive and high in absolute value, thus pointing that the overall process (2) was likely thermodynamically forbidden in the condensed phase. This is was why the formation of such complexes have not been observed so far under conventional conditions. However, the process may be possible under special conditions in the structuring medium like gelatin-immobilized metal hexacyanoferrate(II) template implants [6].

EXPERIMENTAL

Quantum-chemical simulation was performed using the density functional theory method (DFT) combining TZVP standard extended split-valence basis set [10, 11] and OPBE functional [12, 13]; the method has been demonstrated to accurately predict the relation between energy of the states differing in the multiplicity and the basic geometry parameters of 3*d* elements chelates [13–17]. The simulation was performed using GAUSSIAN09 software [18].

The correspondence of the found stationary points to the energy minimum was confirmed by computation

of the energy second derivatives over the atomic coordinates; all the equilibrium structures corresponding to the minima at the potential energy surface possessed only real frequencies (cf. [19, 20]). The following multiplicities were considered: 2, 4, and 6 in the cases of Mn(II) and Co(II); 1, 3, and 5 in the case of Fe(II); 1 and 3 in the cases of Ni(II) and Zn(II); 2 and 4 in the cases of Cu(II). For each ion, the structure with the lowest energy was selected from those optimized at the listed multiplicities. The simulation was performed using the restricted method (RHF) for multiplicity of 1; otherwise, the unrestricted method (UHF) was used. Additionally, the UHF method in combination with a GUESS=Mix option was used for multiplicity of 1; the results were always similar to those obtained using the restricted method.

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