ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 2, pp. 315–319. © Pleiades Publishing, Ltd., 2014.
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Structural Peculiarities of Macrocyclic Chelates, Products of Self-Assembly in the M(II) Ion–2-Amino-2-thioheptanoic Acid–Guanidine–Formaldehyde System, as Shown by Quantum-Chemical Simulation

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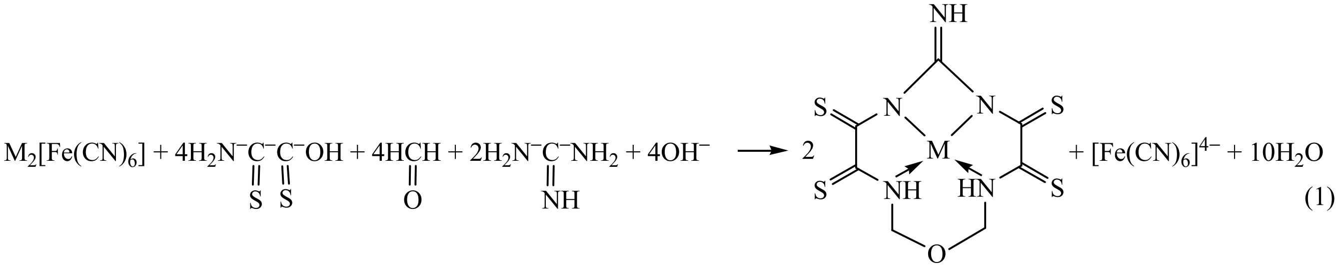
Received March 7, 2013

Abstract—The OPBE/TZVP modification of the DFT method has been applied to compute the geometry parameters of (5456)macrocyclic complexes of M(II) with the (NNNN) tetradentate macrocyclic ligand. The complexes are formed via the template reaction in the quaternary systems including M(II) ion (M = Mn, Fe, Co, Ni, Cu, or Zn), 2-amino-2-thioheptanoic acid, guanidine, and formaldehyde. We report the computed bond lengths, bond angles, and torsion angles in the simulated complexes. Standard enthalpy, entropy, and the Gibbs energy of the complexes formation also have been computed.

DOI: 10.1134/S1070363214020297

Previously we reported on quantum-chemical simulation of a series of (5656)macrocyclic metal chelates of M(II) formed via the self-assembly process (template synthesis) [1–4]. All the studied complexes contained two symmetric 5-membered and two symmetric 6-membered chelate cycles, the chelant being coordinated to M(II) via four nitrogen atoms. Self-assembly can give rise to macrocyclic metal chelates containing three types of chelate cycles [5]. For instance, the (5456)macrocyclic chelates of 3*d* elements M(II) with 7-imino-1-oxa-3,6,8,11-tetraaza-cyclododecan-4,5,9,10-tetrathione (hereinafter referred to as type I complexes) contain a 4-membered, two 5-membered, and a 6-membered chelate cycles; such complexes can be formed in the quaternary systems containing M(II) (M = Mn, Fe, Co, Ni, Cu, or Zn), 2-amino-2-thiohexanoic acid, guanidine, and formaldehyde, see scheme (1).



(1)

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The interest to such combinations of organic compounds (known as ligand synthons) is due to the possibility of their self-assembly into metal chelates containing 4-membered chelate cycles (1); the examples of such coordination compounds are fairly rare. Simulation of the formed chelates of 3*d* elements M(II) ions with the quantum-chemical methods (for example, with the DFT approach) can give important information on the geometry parameters of the unusual complexes.

The computed bond lengths, bond angles, and torsion angles of the type I complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) are collected in Table 1.

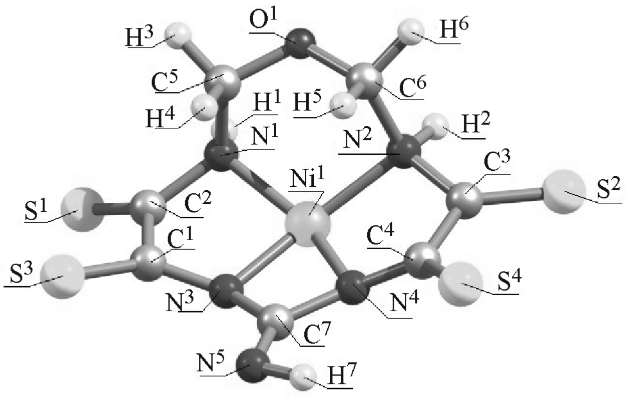
Table 1. Bond lengths, bond angles, and torsion angles in the M(II) complexes of type I

Parameter	Mn	Fe	Co	Ni	Cu	Zn
Bond lengths in the MN_4 chelate node, pm						
M^1–N^1	206.1	202.8	197.7	194.2	207.1	213.7
M^1–N^2	205.3	201.1	197.6	194.2	208.4	220.0
M^1–N^3	188.9	186.7	179.7	182.2	194.5	201.9
M^1–N^4	186.6	182.8	181.9	180.4	196.3	198.2
Bond lengths outside the chelate node, pm						
N^1–C^2	147.8	145.8	146.2	146.5	144.8	147.2
C^2–C^1	149.4	150.9	151.4	150.9	150.7	150.0
C^1–N^3	136.1	134.9	135.1	134.5	133.9	133.0
N^3–C^7	142.2	142.3	142.1	142.0	141.9	142.4
C^7–N^5	126.1	126.1	126.0	126.1	126.4	126.8
C^7–N^4	142.5	142.2	143.0	142.5	142.2	143.0
N^4–C^4	136.2	134.9	134.7	134.1	133.8	133.5
C^4–C^3	147.9	149.8	149.7	150.8	151.0	150.9
C^3–N^2	148.8	147.2	147.6	146.7	144.4	145.2
N^2–C^6	149.8	150.2	149.9	150.2	149.7	149.6
C^6–O^1	140.4	139.9	140.0	142.0	140.1	140.2
O^1–C^5	140.3	140.1	140.2	140.3	140.3	140.4
C^5–N^1	149.8	149.0	149.6	149.8	149.4	149.8
Bond angles in the MN_4 chelate node, deg						
$N^1M^1N^2$	103.1	100.7	103.4	105.0	106.0	101.8
$N^2M^1N^4$	81.9	82.6	85.0	87.1	83.9	81.2
$N^4M^1N^3$	69.0	69.7	71.8	71.7	67.2	66.9
$N^3M^1N^1$	82.4	85.9	87.0	88.4	85.3	84.2
Sum of the bond angles (VAS)	336.4	338.9	347.2	352.2	342.2	334.1
Internal angles in the N_4 moiety, deg						
$N^1N^2N^4$	78.0	79.3	80.5	79.6	77.7	77.0
$N^2N^4N^3$	102.7	103.6	99.5	101.4	103.3	104.8
$N^4N^3N^1$	101.7	98.5	102.1	99.8	101.3	98.4
$N^3N^1N^2$	77.5	78.5	77.4	79.2	77.7	78.8
Sum of the internal angles (NVAS)	359.9	359.9	359.5	360.0	360.0	359.0
Bond angles in the 4-membered chelate cycle, deg						
$M^1N^3C^7$	96.5	96.2	96.4	95.0	96.1	95.1
$N^3C^7N^4$	96.7	95.9	96.1	96.5	99.2	101.2
$C^7N^4M^1$	97.4	97.9	95.1	95.6	96.8	96.5
$N^4M^1N^3$	69.0	69.7	71.8	71.7	67.2	66.9
Sum of the bond angles (VAS^4)	359.6	359.7	359.4	358.8	359.3	359.7
Bond angles in the 5-membered chelate cycle 1, deg						
$M^1N^1C^2$	103.7	98.7	101.3	102.7	100.9	99.6
$N^1C^2C^1$	112.6	111.9	112.4	111.8	111.3	110.4
$C^2C^1N^3$	108.4	106.1	106.1	106.9	108.7	109.8
$C^1N^3M^1$	120.3	116.3	118.6	115.5	131.8	110.4
$N^3M^1N^1$	82.4	85.9	87.0	88.4	85.4	84.2
Sum of the bond angles (VAS^{51})	527.4	518.9	525.4	525.3	517.8	514.4

Table 1. (Contd.)

Parameter	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in the 5-membered chelate cycle 2, deg						
$M^1N^2C^3$	105.7	105.0	105.9	104.6	102.5	100.4
$N^2C^3C^4$	112.5	111.7	111.4	112.0	111.9	111.8
$C^3C^4N^4$	109.5	107.5	107.9	107.2	108.6	108.4
$C^4N^4M^1$	121.6	122.1	120.1	118.4	114.8	116.6
$N^4M^1N^2$	81.9	82.6	85.0	87.1	83.9	81.2
Sum of the bond angles (VAS^{52})	531.2	528.9	530.3	529.3	521.7	518.4
Bond angles in the 6-membered chelate cycle, deg						
$M^1N^1C^5$	102.4	104.0	101.7	100.0	99.7	103.5
$N^1C^5O^1$	111.6	111.0	111.8	111.3	112.2	112.0
$C^5O^1C^6$	117.2	116.8	117.2	117.4	117.4	117.0
$O^1C^6N^2$	111.8	112.1	111.1	111.4	112.0	111.7
$C^6N^2M^1$	102.6	103.1	101.4	99.8	98.9	101.0
$N^2M^1N^1$	103.1	100.7	103.4	105.0	106.0	101.8
Sum of the bond angles (VAS^6)	648.7	647.7	646.6	644.9	646.2	647.0
Torsion angles, deg						
$M^1N^1C^5O^1$	58.9	60.9	60.3	61.3	57.8	56.5
$M^1N^2C^6O^1$	–58.5	–61.4	–61.7	–61.5	–59.0	–58.5
$N^1C^5O^1C^6$	–85.5	–81.3	–80.7	–80.0	–87.9	–89.4
$N^2C^6O^1C^5$	85.2	82.0	81.5	80.3	89.0	91.9
$N^3M^1N^2C^6$	–50.6	–50.1	–54.0	–64.4	–60.4	–56.0
$N^4M^1N^1C^5$	50.0	43.8	55.9	62.3	58.9	52.6
$N^1M^1N^4C^7$	44.4	52.1	37.7	35.8	40.4	48.3
$N^2M^1N^3C^7$	–45.4	–42.8	–47.5	–33.9	–38.5	–42.4
$M^1N^1C^2C^1$	38.1	46.5	39.0	35.4	42.2	45.0
$M^1N^2C^3C^4$	–31.9	–35.6	–30.8	–31.1	–39.7	–43.8
$M^1N^3C^1C^2$	10.7	21.6	18.6	27.4	34.2	36.3
$M^1N^4C^4C^3$	–6.0	–6.9	–19.8	–22.5	–29.8	–30.6
$M^1N^3C^7N^5$	172.9	174.9	171.7	169.9	174.7	175.5
$M^1N^4C^7N^5$	–172.7	–174.8	–171.6	–169.7	–174.8	–175.4
$N^1C^2C^1N^3$	–33.5	–47.8	–39.3	–42.3	–54.1	–58.4
$N^2C^3C^4N^4$	25.9	28.9	33.0	35.4	48.2	52.3
$N^3C^7N^5H^7$	–178.4	–179.2	–177.5	–178.9	–179.9	–178.6
$N^4C^7N^5H^7$	–1.4	–1.5	–0.6	–0.1	2.5	1.8

Spatial structures of the complexes were similar, the Ni(II) chelate is given as representative example. All complexes were non-coplanar, the donor ligand centers are arranged in the shape of pyramid around the metal ion: sum of the four bond angles $N^1M^1N^2$, $N^2M^1N^4$, $N^4M^1N^3$, and $N^3M^1N^1$ (VAS) was 336.4°–347.2°. Sum of the internal (nonbond) angles in the $N^1N^2N^3N^4$ tetragons (NVAS) was close to 360.0° in all studied complexes; hence, this group of atoms was planar. Noteworthily, only two of the listed bond angles ($N^2M^1N^4$ and $N^3M^1N^1$) were close in value; the same was true in the case of the internal angles (Table 1). The metal–nitrogen bond lengths *d*(M–N) were not equal as well, however, some of them were close pairwise. The *d*(M–N) lengths were significantly longer in the cases of two nitrogen atoms forming the 6-membered ring as compared to those forming the 4-membered ring. The shortest M–N bonds were found in the Ni(II) complex, whereas the Zn(II) complex contained the longest M–N bonds. In the series of Mn, Fe, Co, Ni, Cu, and Zn complexes, *d*(M–N) decreased from Mn to Ni and increased from Ni to Zn (Table 1).



Spatial structure of the Ni(II) complex of type I.

In the 4-membered metal chelate cycles, nitrogen donor atoms were almost coplanar with the carbon and metal atoms, although the sum of bond angles VAS^4 in all cases deviated from the sum of internal angles in the planar tetragon (the highest deviation was of 1.2°). Deviation from planarity was more significant in both 5-membered chelate cycles: the corresponding sum of bond angles, VAS^{51} and VAS^{52}, deviated from the sum of internal angles in the planar pentagon by at least 10° (Table 1). Noteworthily, in all the studied complexes, the 5-membered cycles were not identical: the corresponding bond angles and their sums were different. The 6-membered cycles were non-planar: the sum of bond angles VAS^6 deviated from that in the planar hexagon by at least 70° (Table 1). The respective bond angles in the chelate cycles as well at out of them were not pairwise equal, the respective bond lengths were different as well. The bond angles were not sensitive to the nature of the complex forming ion M(II). The majority of torsion angles significantly deviated from either 0° or 180°, thus confirming the non-planarity of the studied complexes (Table 1).

Table 2. Standard enthalpy $\Delta H^0_{\mathrm{f,\,298}}$, entropy $S^0_{\mathrm{f,\,298}}$, and the Gibbs energy $\Delta G^0_{\mathrm{f,\,298}}$ of type I chelates formation

M	$\Delta H^0_{\mathrm{f,\,298}}$, kJ/mol	$S^0_{\mathrm{f,\,298}}$, J mol^{-1} K^{-1}	$\Delta G^0_{\mathrm{f,\,298}}$, kJ/mol
Mn	380.1	691.1	315.7
Fe	513.9	693.5	447.4
Co	547.0	689.3	482.7
Ni	537.5	683.5	474.8
Cu	669.4	690.0	605.8
Zn	571.5	685.4	511.8

According to the simulation data, spin quartet was the ground state of the Mn(II) complex, it was intermediate between the low-spin and the high-spin complexes. The same was true for the Fe(II) complex with the triplet ground state. In the cases of low-spin Co(II) and Ni(II) complexes, the ground states were spin spin doublet and spin singlet, respectively. The Cu(II) and Zn(II) complexes possessed spin doublet and singlet, respectively, as the ground states. The energy difference between the ground state of the complexes and the higher multiplicity states was 13.0 [sextet, Mn(II)], 26.3 [quintet, Fe(II)], 40.5 [quartet, Co(II)], 67.0 [triplet, Ni(II)], 61.9 [quartet, Cu(II)], and 53.0 [triplet, Zn(II)] kJ/mol. As seen from the listed values, the ground states of the complexes were significantly more favorable than those of the higher multiplicity.

All studied macrotricyclic chelates were asymmetric. The asymmetry was largely due to the fact that, contrary to the expectations, the distances between the H^9 hydrogen (that of the imine group adjacent to the C^7 carbon of the 4-membered cycle) and the nitrogen atoms N^5 and N^6 were different [the H^7–N^3 and H^7–N^4 distances were, respectively, 324.4 and 259.1 pm in the case of Mn(II), of 324.9 and 260.3 pm in the case of Fe(II), of 324.4 and 261.4 pm in the case of Co(II), of 324.8 and 261.2 pm in the case of Ni(II), of 324.1 and 260.0 pm in the case of Cu(II), and of 323.6 and 257.2 pm in the case of Zn(II)]. Due to the structural asymmetry, relatively high dipole moments μ could be expected for all the studied complexes. Indeed, the computed dipole moments were 8.24 [Mn(II)], 7.64 [Fe(II)], 7.66 [Co(II)], 7.93 [Ni(II)], 8.23 [Cu(II)], and 9.28 [Zn(II)] D. Noteworthily, the most asymmetric complexes, those of Cu(II) and Zn(II), possessed the highest dipole moments.

The key thermodynamic parameters of the studied metal chelates (standard enthalpy, entropy, and Gibbs energy of formation) are collected in Table 2. All functions were positive; therefore, the type I complexes could not be formed directly from elementary substances. Consequently the above described overall process (1) is likely to occur via the template process in gelatin-immobilized matrix implants [5].

The quantum-chemical simulation discussed above was performed in the frame of density functional theory approach combining the TZVP split-valence basis set [6, 7] with the OPBE functional [8, 9]. According to the data presented in [9–13], that method reliably predicted the energy difference between the various multiplicity states as well as the geometry parameters of complexes of 3*d* elements. The simulation was performed using GAUSSIAN09 software [14]. Similarly to [15–17], the correspondence of the found stationary points to the energy minima was proved by calculation of the energy second derivatives over the atomic coordinates; all frequencies were found to be positive. The following multiplicities were considered: 2, 4, and 6 [Mn(II) and Co(II)]; 1, 3, and 5 [Fe(II)]; 1 and 3 [Ni(II) and Zn(II)]; 2 and 4 [Cu(II)]. The state with the lowest energy was considered to be the ground state. The simulation of the singlet state was performed by the restricted method, whereas other multiplicity states were simulated by the unrestricted method. In the case of the singlet states, the result of computation by the restricted method was identical to that by the unrestricted method with the GUESS=Mix option. The $\langle S^2 \rangle$ parameter of the favorable by energy multiplicity state was 4.4258 [Mn(II), ground state multiplicity = 4], 2.1649 [Fe(II), 3], 0.7553 [Co(II), 2], 0.0000 [Ni(II) and Zn(II), 1]. The excited states were not studied.

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (project no. 09-03-97001). Quantum-chemical simulations were performed at Kazan Branch of Joint Supercomputer Center of the Russian Academy of Sciences.

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