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Quantum-Chemical Simulation of Structure of Isomeric Asymmetric (555)Macrotricyclic Chelates of 3*d* Elements Arising via Self-Assembly in Quaternary Systems Metal(II)–Ethanedithioamide–Hydrazinomethanethioamide–Ethanedial

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Abstract—We utilized the OPBE/TZVP (GAUSSIAN-09) hybrid density functional method to compute thermodynamic (full energy; standard enthalpy, entropy, and Gibbs energy of formation) and geometry (bond lengths, bond angles, and torsion angles) parameters of (555)macrotricyclic complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with (NSSN) coordination of the ligand donor centers. Such complexes can be formed upon interaction of hexacyanoferrate(II) of the listed metals, ethanedithioamide, hydrazinomethanethioamide, and ethanedial in gelatin-immobilized matrix implants. Complexes of Cu(II) and Zn(II) are slightly nonplanar, the other complexes are almost flat. In all cases the additionally formed five-membered cycle is practically flat.

Keywords: template synthesis, macrocyclic ligand, molecular structure, quantum-chemical simulation, density functional theory

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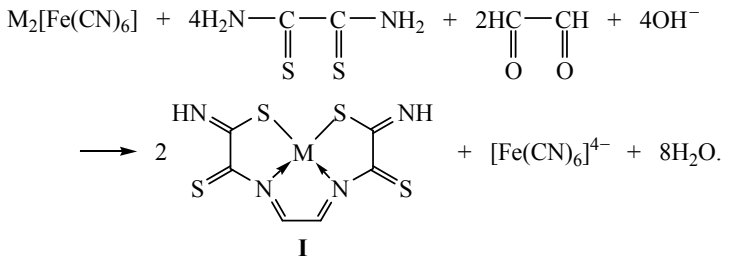
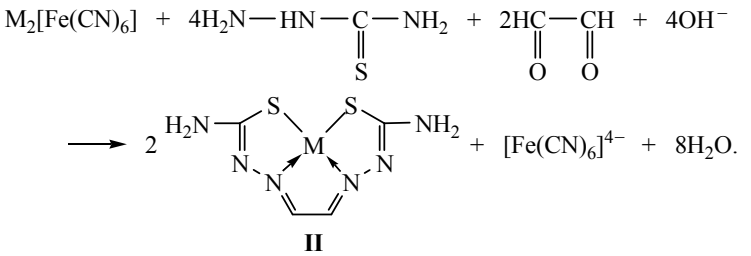
In earlier studies, we experimentally discovered a self-assembly process in the tertiary systems of M(II)–ethanedithioamide–ethanedial (M = Ni or Cu) occurring in the gelatin-immobilized matrices of metal M hexacyanoferrate(II) [1, 2]. According to ESR and magnetic susceptibility data, the (565)macrotricyclic complexes of type **I** were thus formed [scheme (1)].

In [3] we performed quantum-chemical simulation of molecular structure of the complexes formed in the said systems applying the density functional method (DFT) and found some specific features of coordination of the formed macrotricyclic ligand with 3*d* metal ions, in particular, with Ni(II) and Cu(II). Further, we performed similar simulation to study the formation of the type **II** complexes in the M(II)–hyd-razinomethanethioamide–ethandial systems via the scheme (2) [4].

Self-assembly of two asymmetric isomers of (555)macrotricyclic metal chelates **III** and **IV** is possible

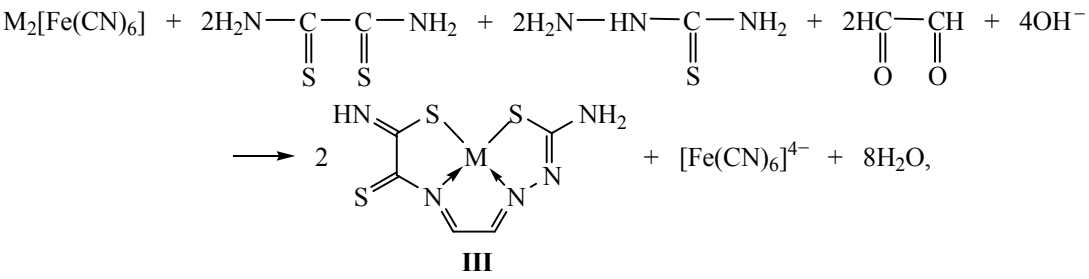


I (1)



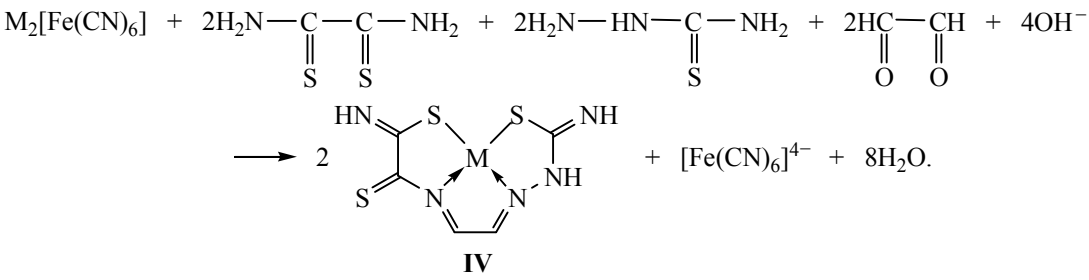
II

(2)



III

(3)



IV

(4)

in the quaternary systems containing the both above-mentioned N,S-ligands and ethanedial.

In this work we performed quantum-chemical DFT simulation of those complexes. To the best of our knowledge (see review [5]), a simulation of such structures has not been reported so far.

It was first rational to estimate which of the complexes (**III** or **IV**) possessed the lower full energy in the case of each of the ions(II) in the Mn–Zn series. The simulated full energies *E* with accounting for zero vibrations are collected in Table 1. In the cases of all considered ions M(II) the *E*(**IV**) > *E*(**III**) relation held, full energy difference between the isomeric complexes being of no less than 20 kJ/mol [schemes (3), (4)].

The data on relative complexes stability presented in Table 1 refer to the gas phase. Nevertheless, taking into account the special features of the discussed chelating ligand and the M(II) ions it was reasonable to suggest that parameters of the complex formation in condensed phase were not qualitatively different. Indeed, the energy difference between complexes **III** and **IV** in the condensed state obtained via the PCM quantum-chemical simulation [6] were practically equal to those shown in Table 1. However, the PCM method for condensed phase does not presume geometry optimization; as geometry is the key factor influencing the energy parameters, we consider the data on relative full energy of complexes **III** and **IV** as determined by PCM method less reliable in comparison with the corresponding OPBE/TZVP gas phase results.

Hereinafter we will discuss molecular structures of the more stable complexes **III**.

The simulated bond lengths, bond angles, and torsion (dihedral) angles in the type **III** complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) are collected in Table 2. Spatial structures of the selected complexes are given in Figs. 1 and 2; the atoms numeration is also illustrated by the figures.

For four M(II) ions of the studied six, the coordination of the ligand donor centers with respect to the metal ion was ideally flat: VAS, the sum of four bond angles $S^1M^1S^3$, $S^3M^1N^3$, $N^3M^1N^2$, and $N^2M^1S^1$, formed by the donor atoms and the metal ion was

Table 1. Total energy of complexes **III** and **IV** of different metals M in the gas phase with accounting for zero vibrations[a]

M(II)	*E* (**III**)	*E* (**IV**)
Mn(II)	–2812.949814	–2812.928378
	(0.0)	(56.3)
Fe(II)	–2925.705218	–2925.684169
	(0.0)	(55.3)
Co(II)	–3044.820150	–3044.795472
	(0.0)	(64.8)
Ni(II)	–3170.444030	–3170.418971
	(0.0)	(65.8)
Cu(II)	–3302.644420	–3302.618719
	(0.0)	(67.5)
Zn(II)	–3441.546282	–3441.538601
	(0.0)	(20.2)

[a] Values without parentheses: total energy in the Hartree units; values in parentheses: relative energy in kJ/mol. In the latter case, zero corresponds to the total energy of the complex with the lowest energy.

exactly 360°. The two exceptions were the complexes of Cu(II) and Zn(II), however, in those cases the said angles sum was also only slightly higher (361.3° and 360.6°, respectively). NVAS, sum of the interior (non bond) angles $S^1S^3N^3$, $S^3N^3N^2$, $N^3N^2S^1$, and $N^2S^1S^3$ in the studied complexes was either equal to 360.0° [Mn(II), Fe(II), Co(II), and Ni(II)] or very close to that value [357.1° in the case of Cu(II) and 358.5° in the case of Zn(II)]. Hence, the donor atoms group N_2S_2 in the majority of the studied complexes was practically flat as well. Noteworthily, in each of the studied complexes all four bond angles $S^1M^1S^3$, $S^3M^1N^3$, $N^3M^1N^2$, and $N^2M^1S^1$ were different; the same was true for the $S^1S^3N^3$, $S^3N^3N^2$, $N^3N^2S^1$, and $N^2S^1S^3$ non bond angles (Table 2). Lengths of the M–N and M–S bonds were different as well. The bond lengths changed non-monotonously in the Mn–Zn series, being minimal in the case of Ni(II); in all cases, the M–S bonds were significantly longer that the M–N ones.

A special feature of the studied complexes **III** is that even though the above-listed bond angles, non bond angles, and bond lengths were unequal, in all complexes the 5-membered chelate cycles containing the donor sulfur and nitrogen atoms were practically planar: the corresponding sums of bond angles VAS[51] and VAS[52] were either equal to sum of interior angles in a planar pentagon 540° [Mn(II), Fe(II), Co(II), and Ni(II)] or very close to that value [Cu(II) and Zn(II)] (Table 2). Consequently the VAS[53] sum on the bond angles showed that those 5-membered cycles were practically planar as well. Nevertheless, in all studied chelates the mentioned metal cycles were significantly

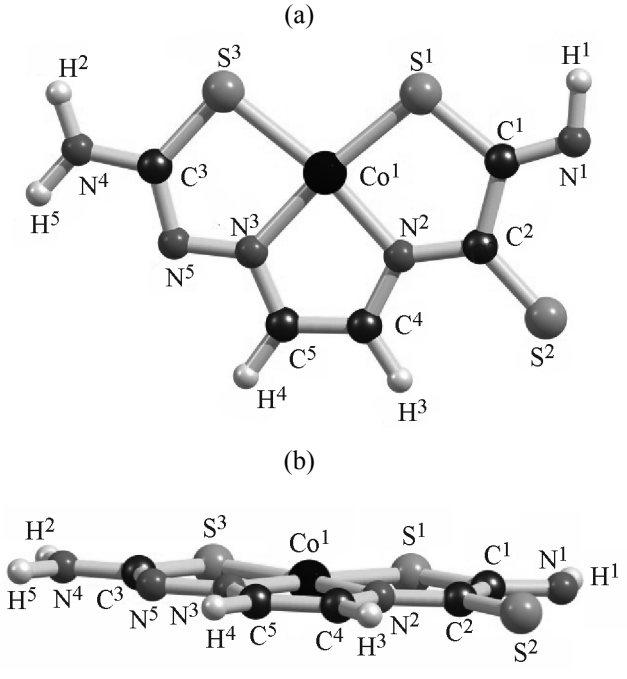


Fig. 1. Spatial structure of Co(II) complex **III**: (a) front view and (b) side view.

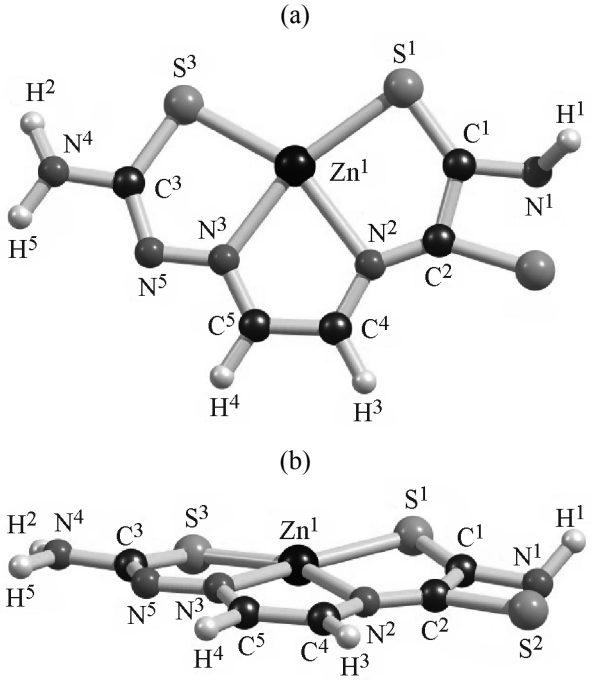


Fig. 2. Spatial structure of Zn(II) complex **III**: (a) front view and (b) side view.

Table 2. Bond lengths, bond angles, and torsion angles in complexes **III** of different metals M

M	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in the MN_2S_2 chelate node, pm						
$M^1–N^2$	196.8	190.8	190.2	188.0	196.6	223.3
$M^1–N^3$	194.9	186.8	184.7	183.0	195.7	212.1
$M^1–S^1$	220.9	214.5	212.5	210.4	219.8	239.1
$M^1–S^3$	229.6	219.9	220.7	217.7	225.9	231.4
Selected bond lengths out of chelate node, pm						
$S^1–C^1$	180.3	179.7	179.3	178.7	177.1	170.5
$C^1–C^2$	150.6	150.5	150.3	150.1	150.7	140.0
$C^2–N^2$	137.5	138.2	137.9	137.8	136.6	130.8
$N^2–C^4$	136.1	135.5	134.2	133.9	133.4	130.9
$C^4–C^5$	138.1	138.4	139.0	139.1	140.3	143.5
$C^5–N^3$	135.2	135.3	135.0	134.7	133.3	130.7
$N^3–N^5$	133.6	133.7	132.2	131.7	130.7	133.0
$N^5–C^3$	132.4	132.9	134.6	134.8	135.2	133.2
$C^3–S^3$	175.8	176.4	173.5	173.2	173.2	175.1
$C^1–N^1$	127.1	127.4	127.4	127.4	127.7	139.3
$C^2–S^2$	165.0	164.8	165.0	164.8	165.1	180.1
$C^3–N^4$	134.7	134.3	134.3	134.2	134.5	135.4
Bond angles in MN_2S_2 chelate node, deg						
$S^1M^1S^3$	109.6	103.1	101.8	99.9	107.0	115.4
$S^3M^1N^3$	82.5	85.3	85.7	86.5	84.4	83.0
$N^3M^1N^2$	81.9	83.8	84.9	85.5	82.9	74.1
$N^2M^1S^1$	86.0	87.8	87.6	88.1	87.0	88.1
Sum (VAS)	360.0	360.0	360.0	360.0	361.3	360.6
Non bond angles in N_2S_2 group, deg						
$S^1S^3N^3$	77.8	80.2	79.9	80.8	78.9	78.5
$S^3N^3N^2$	103.4	101.2	101.1	100.1	100.5	105.8
$N^3N^2S^1$	99.3	97.8	96.2	95.6	97.7	98.7
$N^2S^1S^3$	79.5	81.6	82.8	83.5	80.0	75.5
Sum (NVAS)	360.0	360.0	360.0	360.0	357.1	358.5
Bond angles in the 5-membered chelate cycle 1, deg						
$M^1S^1C^1$	100.4	100.3	100.8	100.8	99.3	90.3
$S^1C^1C^2$	116.0	115.3	115.0	114.7	117.3	129.1
$C^1C^2N^2$	112.9	112.1	111.8	111.6	113.1	124.0

Table 2. (Contd.)

M	Mn	Fe	Co	Ni	Cu	Zn
Bond angles in the 5-membered chelate cycle 1, deg						
$C^2N^2M^1$	124.7	124.5	124.8	124.8	122.6	108.0
$N^2M^1S^1$	86.0	87.8	87.6	88.1	87.1	88.1
Sum (VAS^{51})	540.0	540.0	540.0	540.0	539.4	539.5
Bond angles in the 5-membered chelate cycle 2, deg						
$M^1S^3C^3$	94.8	94.4	93.9	93.8	93.7	94.2
$S^3C^3N^5$	124.4	123.3	123.5	123.3	125.3	128.2
$C^3N^5N^3$	111.4	110.2	110.2	110.0	111.2	118.1
$N^5N^3M^1$	126.8	126.7	126.7	126.4	124.7	120.9
$N^3M^1S^3$	82.6	85.4	85.7	86.5	84.4	83.0
Sum (VAS^{52})	540.0	540.0	540.0	540.0	539.3	539.4
Bond angles in the 5-membered chelate cycle 3, deg						
$M^1N^2C^4$	112.3	112.1	111.2	111.0	110.7	114.1
$N^2C^4C^5$	116.5	115.6	116.1	116.1	117.7	116.6
$C^4C^5N^3$	115.3	114.1	114.0	113.7	115.2	117.6
$C^5N^3M^1$	114.0	114.4	113.8	113.7	112.7	117.5
$N^3M^1N^2$	81.9	83.8	84.9	85.5	82.9	74.1
Sum (VAS^{53})	540.0	540.0	540.0	540.0	539.2	539.9
Bond angles out of the chelate cycles, deg						
$S^1C^1N^1$	123.2	124.3	124.4	124.5	124.2	130.8
$N^1C^1C^2$	120.8	120.4	120.6	120.8	118.6	100.1
$S^2C^2C^1$	122.1	122.9	122.9	123.1	122.6	92.5
$C^2N^2C^4$	122.9	123.3	124.0	124.2	126.1	137.7
$C^5N^3C^5$	119.2	118.9	119.5	119.9	122.3	121.4
$N^5C^3N^4$	117.7	117.8	116.1	116.1	115.1	115.3
$S^3C^3N^4$	117.9	118.9	120.3	120.6	119.6	116.5
$H^1N^1C^1$	111.4	110.4	110.7	111.0	111.4	118.2
$H^2N^4C^3$	120.8	120.6	120.7	120.9	120.7	119.6
$H^5N^4C^3$	119.2	119.7	119.5	119.4	119.3	117.9
$H^2N^4H^5$	119.7	119.7	119.8	119.7	119.9	119.4
Torsion (dihedral) angles, deg						
$S^3M^1N^2C^4$	0.3	0.0	0.0	0.0	–44.2	–20.4
$S^1M^1N^3C^5$	0.0	0.1	0.1	0.1	–42.8	–23.7
$M^1N^2C^4C^5$	0.0	0.0	0.0	0.0	10.0	1.1

Table 2. (Contd.)

M	Mn	Fe	Co	Ni	Cu	Zn
Torsion (dihedral) angles, deg						
$M^1N^3C^5C^4$	0.0	0.0	0.0	0.0	1.9	3.1
$N^2C^4C^5N^3$	0.0	0.0	0.0	0.0	–8.2	–2.8
$S^3M^1N^2C^2$	–179.7	–180.0	–180.0	–180.0	143.9	163.6
$N^3M^1S^1C^1$	0.0	–0.1	–0.1	–0.1	49.8	25.3
$M^1N^2C^2C^1$	0.0	0.0	0.0	0.0	9.0	–0.8
$M^1S^1C^1C^2$	0.0	0.0	0.0	0.0	–1.9	–7.0
$S^1C^1C^2N^2$	0.0	0.0	0.0	0.0	–3.7	6.4
$S^1M^1N^3N^5$	179.9	–179.9	–179.9	–179.9	143.0	161.6
$M^1N^3N^5C^3$	0.1	0.0	0.0	0.0	–3.7	1.9
$M^1S^3C^3N^5$	0.2	0.0	0.0	0.0	–8.8	–7.0
$S^3C^3N^5N^3$	–0.2	0.0	0.0	0.0	9.1	4.3
$M^1S^1C^1N^1$	180.0	–180.0	–180.0	–180.0	179.7	172.0
$M^1S^3C^3N^4$	–179.4	180.0	–179.9	180.0	172.9	172.8
$N^1C^1C^2S^2$	0.0	0.0	0.0	0.0	–6.9	5.9
$N^1C^1C^2N^2$	–180.0	180.0	–180.0	180.0	174.8	–172.8
$N^4C^3N^5N^3$	179.4	–180.0	179.9	–180.0	–172.6	–175.5
$S^1M^1S^3C^3$	179.9	180.0	180.0	180.0	–167.1	–170.3
$S^3M^1S^1C^1$	179.9	180.0	180.0	180.0	–167.4	–169.6

different, as evidenced by the bond angles. Torsion angles in the complexes Mn(II), Fe(II), Co(II), and Ni(II) were close to either 0° or 180°, so they were practically flat; in the cases of Cu(II) and Zn(II) complexes the torsion angles were noticeably deviating from those values, hence, these two complexes were non-planar (Table 2). Noteworthily, the values of the corresponding angles or bond lengths were only slightly dependent on the M(II) nature; some specific features were found in the case of Zn(II) complex. For instance, the C^5–N^3 bond length was 135.2 (Mn), 135.3 (Fe), 135.0 (Co), 134.7(Ni), 133.3 (Cu), and 130.7 pm (Zn), and the $C^1C^2N^2$ bond angle was of 112.9° (Mn), 112.9° (Fe), 111.8° (Co), 111.6° (Ni), 113.1° (Co), and 124.0° (Zn).

As documented by Figs. 1 and 2, the considered (555)macrotricyclic chelates had a single symmetry plane (if any); as they were not centrosymmetric, fairly high dipole moment was anticipated for those complexes. Indeed, the complexes dipole moments computed with the OPBE/TZVP method were 7.90 (Mn), 8.32 (Fe), 8.48 (Co), 8.43 (Ni), and 7.96 D (Cu). Noteworthily, dipole moment of the zinc complex was much lower, 2.73 D.

Table 3 contains thermodynamic parameters of formation of the studied metal chelates: standard enthalpy, entropy, and Gibbs energy. In all cases, the mentioned parameters were positive and quite high; in particular, the positive $\Delta_f G^0_{298}$ value evidenced that the formation of complexes **III** from elemental substances was impossible, and the overall process of the complex formation shown in the scheme above was likely thermodynamically forbidden in the solution and in the solid phase (that was indeed confirmed experimentally). However, under special conditions of complex formation in the pre-organized systems (like the gelatin matrices [5]) the discussed process is possible.

Table 3. Standard enthalpy, entropy, and Gibbs energy of formation of the complexes **III** of different metals M

M	$\Delta_f H^0_{298}$, kJ/mol	$\Delta_f S^0_{298}$, J mol^{-1} K^{-1}	$\Delta_f G^0_{298}$, kJ/mol
Mn	166.7	597.7	104.8
Fe	309.4	590.5	248.2
Co	360.5	579.8	303.4
Ni	364.1	576.8	307.8
Cu	516.0	581.0	459.5
Zn	432.9	583.0	378.3

According to the simulation results, the ground state of Mn(II) was spin quartet, and it was an intermediate situation between the high-spin (sextet) and the low-spin (doublet) states. The same was true in the case of Fe(II) complex, its ground state being triplet. The ground states of the Co(II) and Ni(II) complexes were spin doublet and singlet, respectively, i.e. those complexes were low-spin ones. The ground states of the Cu(II) and Zn(II) complexes were spin doublet and singlet, respectively. The energy difference between the ground state and the closest excited spin state was 24.1 (Mn, sextet), 51.5 (Fe, quintet), 35.8 (Co, quartet), 73.3 (Cu, quartet), 64.8 (Ni, triplet), and 4.1 (Zn, triplet) kJ/mol (multiplicity of the corresponding excited state is given in parentheses). In the case of the Zn(II) complex the energy difference was small, and the spin-crossover (spin isomerism) phenomenon can be expected.

EXPERIMENTAL

Quantum-chemical simulation was performed in the frame of density functional theory approach combining the TZVP standard split-valence basis set [7, 8] with the OPBE functional [9, 10]. According to the data presented in [10–14], this 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 [15]. Similarly to [16–18], the correspondence of the found stationary points to the energy minima was confirmed by the 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 one. Simulation of the singlet state was performed by the restricted (RHF), whereas other multiplicity states were simulated by the unrestricted (UHF) Hartree–Fock 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.

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