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Quantum Chemical Calculation of the Molecular Structures of (666)Macrotricyclic Chelates of 3*d* Elements in the M(II)–Propanedithioamide–Formaldehyde Systems by the Density Functional Theory Method

O. V. Mikhailov and D. V. Chachkov

[a] *Kazan National Research Technological University, ul. Marksa 68, Kazan, 420015 Russia*
[b] *Joint Supercomputer Center, Kazan Branch, Russian Academy of Sciences, ul. Lobachevskogo 2/31, Kazan, Tatarstan, 420111 Russia*
e-mail: ovm@kstu.ru

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Abstract—The nonhybrid OPBE/TZVP density functional theory (DFT) method and the Gaussian09 program package were used to calculate the thermodynamic and geometric parameters of asymmetric macrocyclic M(II) complexes with three six-membered metal rings and (NNNN)-coordination of the donor sites of the ligand. The complexes are formed upon self-assembly (template synthesis) of hexacyanoferrates(II) of the corresponding M(II), propanedithioamide $H_2N–C(=S)–CH_2–C(=S)–NH_2$, and formaldehyde $H_2C(=O)$ in gelatin-immobilized matrix implants. Note that complexes of this type are formed only for M = Ni, Cu, and Zn, while for M = Mn, Co, and Fe, these compounds are unstable. Bond lengths and bond and torsion angles are presented. In each of these complexes, both the MN_4 chelate units and the N_4 units and all six-membered metal rings were found to be non-coplanar.

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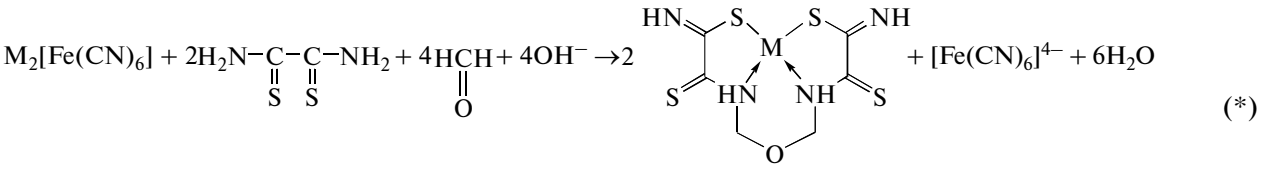
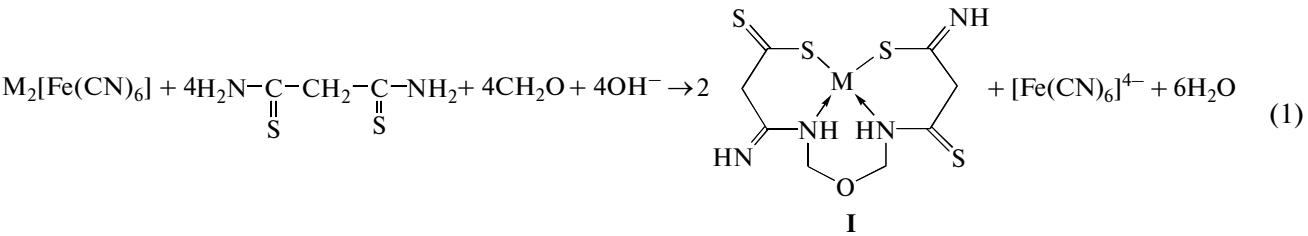
Previously [1] we performed quantum chemical calculation for (565)macrotricyclic chelates of some M(II) ions of 3*d* elements formed upon template reactions in the M(II)–ethanedithioamide $H_2N–C(=S)–C(=S)–NH_2$–formaldehyde $H_2C(=O)$ systems in metal hexacyanoferrate(II) gelatin-immobilized matrix implants according to the overall scheme:

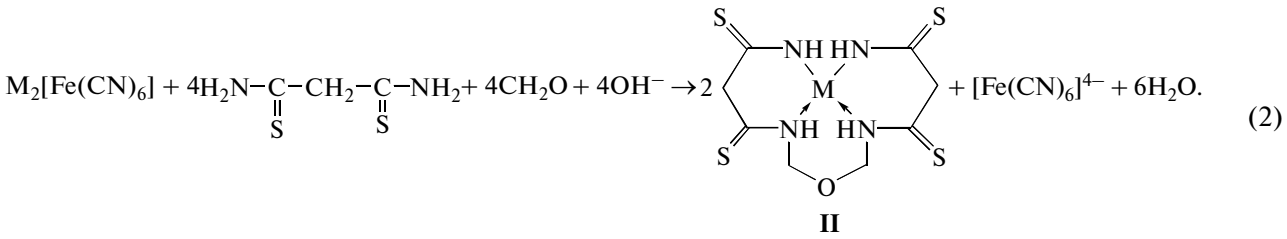


(M = Mn, Fe, Co, Ni, Cu, Zn).

If dithiooxamide in this ternary system is replaced by its analog, propanedithioamide, the formation of two types of (666)macrotricyclic metal chelates **I** and **II** can in principle be expected, according to overall schemes (1) and (2), respectively:



I



(2)

II

These complexes are mentioned in a review [2]; in an earlier work [3], template synthesis in the Cu(II)–propanedithioamide-formaldehyde system in copper(II) hexacyanoferrate(II) gelatin-immobilized matrix was experimentally carried out and a chelate was isolated that could be identified as either **I** or **II** with the same probability. Unfortunately, the authors were unable to perform an X-ray diffraction study of this compound because it was isolated as very fine crystals unsuitable for single-crystal X-ray diffraction. Therefore, the question of whether metal chelates of types **I** and **II** or either of them can form in the M(II)–propanedithioamide–formaldehyde ternary systems remains open. To solve this problem and predict the feasibility of processes (1) and (2) in the M(II)–propanedithioamide–formaldehyde systems, it is pertinent to carry out quantum chemical calculation for metal complexes **I** and **II** by already tested [4–10] OPBE/TZVP density functional theory method, which provides independent objective data on their total energy (E) and standard enthalpy ($\Delta H^0_{f,298}$), entropy ($S^0_{f,298}$), and Gibbs energy ($\Delta G^0_{f,298}$) of formation and on geometric parameters of the structures (bond lengths, bond angles, and torsion angles). This issue is the subject of the present communication.

CALCULATION DETAILS

The quantum chemical calculations were performed by the density functional theory (DFT) method with the standard extended split-valence TZVP basis set [11, 12] and non-hybrid OPBE functional [13, 14]. According to [14–18], in the case of complexes of 3*d* elements, this method gives a fairly accurate relative energy stabilities of high- and low-spin states and simultaneously it reliably characterizes the key geometric parameters of the molecular structures of these compounds. The calculations were carried out by the Gaussian09 program package [19]. As in our previous works, in particular, in [4–10], the correspondence of the found stationary points to energy minima was proved in all cases by calculation of the second derivatives of energy with respect to the atom coordinates; all equilibrium structures corresponding to minimum points in the potential energy surface had only positive frequency values.

RESULTS AND DISCUSSION

The performed OPBE/TZVP DFT quantum chemical calculations of (666)macrotricyclic complexes of types **I** and **II** provided quite an unexpected result. For complexes of type **I** with the MN_2S_2 chelate unit for M = Mn, Fe, Co, Ni, Cu, and Zn, attempts at geometry optimization result in structures having no physical meaning (for example, for M = Mn, the CN of Mn in the resulting structure was 6, and it contained two three-membered, one five-membered, and one six-membered rings). As regards type **II** complexes with the MN_4 chelate unit, according to our calculation results, they can exist only for Ni(II), Cu(II), and Zn(II). The attempts of geometry optimization for structure **II** for M = Mn, Fe, and Co results in structures having no physical meaning. Although our data on the relative stability of **I** and **II** refer to the gas phase, nevertheless, in view of the specific properties of both the ligand formed and M(II) ions, no significant changes are to be expected for condensed media, at least qualitatively. The PCM quantum chemical calculation that we carried out for the above-indicated (666)macrotricyclic complexes [20] in the condensed state confirmed this conclusion (note that since the PCM technique does not imply the geometry optimization of the complexes, the computation results obtained by this method appear less reliable than OPBE/TZVP DFT data for the gas phase).

By analogy with molecular structures of (565)macrotricyclic metal chelate, which were shown [1, 21, 22] to be non-coplanar and asymmetric, one can expect that the same will be true for the molecular structures of the (666)macrotricyclic chelates under consideration. Our calculations of the molecular structures of M(II) complexes of type **II** (M = Ni, Cu, Zn) confirm the above theoretical expectations. The molecular structures of the complexes are shown in Figs. 1–3; the key parameters of these structures (bond lengths and bond and torsion angles) are summarized in Table 1. As can be seen from Figs. 1–3, the macrotricyclic chelates in question do not have any symmetry elements; due to the absence of a center of symmetry, they are expected to have rather high electric dipole moments (μ). The OPBE/TZVP calculation gives μ of 7.06 for the Ni(II) complex, 7.47 for the Cu(II) complex, and 8.09 Debye units for the Zn(II) complex. Interestingly, the most asymmetric of these complexes, particularly the Ni(II) chelate, has a lower μ value than the other two complexes.

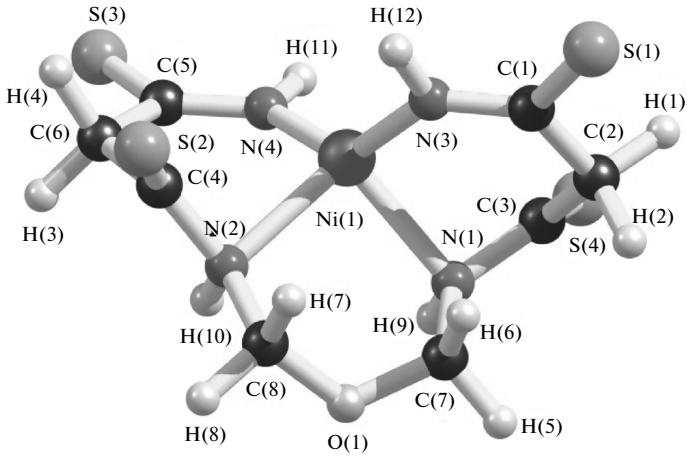


Fig. 1. Spatial structure of Ni(II) complex of type **II**.

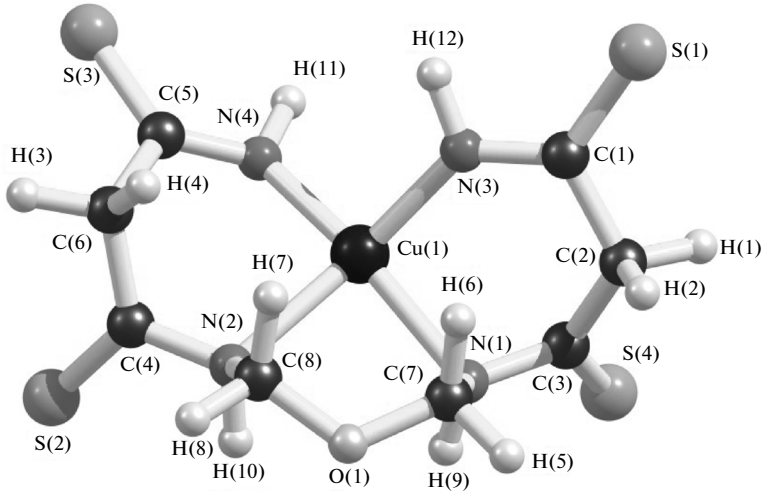


Fig. 2. Spatial structure of Cu(II) complex of type **II**.

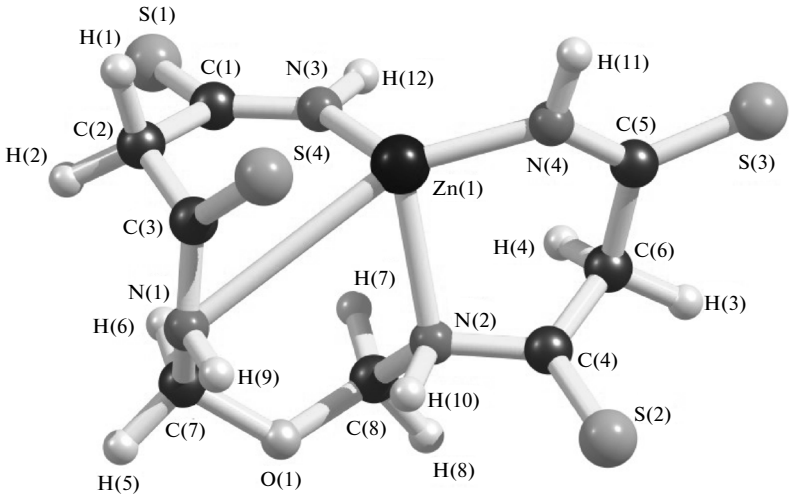


Fig. 3. Spatial structure of Zn(II) complex of type **II**.

Table 1. Bond lengths and bond and torsion angles in Ni(II), Cu(II), and Zn(II) chelates of type **II**

M	Ni	Cu	Zn
Bond lengths in the MN_4 chelate unit, pm			
M1N1	211.7	214.4	331.4
M1N2	212.3	221.9	227.8
M1N3	188.8	196.7	197.3
M1N4			
Selected bond lengths outside the MN_4 chelate unit, pm			
N1C3	140.9	141.2	134.4
C3C2	149.8	149.4	148.8
C2C1	152.9	153.3	155.2
C1N3	132.9	131.9	132.6
N2C4	140.2	141.8	143.7
C4C6	150.7	149.2	149.2
C6C5	152.7	154.5	155.9
C5N4	133.1	131.9	133.2
N1C7	148.0	148.5	145.6
C7O1	140.0	140.0	141.2
O1C8	140.4	140.1	140.5
C8N2	146.8	149.1	150.8
C1S1	167.7	168.4	166.8
C4S2	165.3	164.4	164.1
C5S3	167.7	168.0	166.5
C3S4	165.1	164.7	171.5
Bond angles in the MN_4 chelate unit, deg			
N1M1N2	90.2	84.8	63.8
N2M1N4	89.5	92.7	96.2
N4M1N3	136.6	100.2	118.3
N3M1N1	91.9	89.7	80.7
BAS	408.2	367.4	359.0
Interior angles in the N_4 group, deg			
N1N2N4	73.1	85.8	111.3
N2N4N3	65.9	82.2	62.1
N4N3N1	65.1	86.8	95.8
N3N1N2	72.7	85.0	60.0
NBAS	276.8	339.8	329.2
Bond angles in six-membered chelate ring 1, deg			
M1N1C3	96.8	102.7	49.8
N1C3C2	117.2	116.9	119.1
C3C2C1	116.9	116.8	115.5
C2C1N3	117.1	118.3	114.8
C1N3M1	131.7	133.0	130.4
N3M1N1	91.9	89.7	80.7
BAS[61]	671.6	677.4	610.3
Bond angles in six-membered chelate ring 2, deg			
M1N2C4	91.2	109.3	103.6
N2C4C6	113.4	116.5	116.4
C4C6C5	117.8	110.9	111.7
C6C5N4	116.9	116.6	115.3
C5N4M1	128.1	127.7	125.9
N4M1N2	89.5	92.7	96.2
BAS[62]	656.9	673.7	669.1

Table 1. (Contd.)

M	Ni	Cu	Zn
Bond angles in six-membered chelate ring 3, deg			
M1N1C7	109.8	104.5	106.3
N1C7O1	110.7	110.5	110.6
C7O1C8	116.2	117.3	118.6
O1C8N2	110.6	109.5	110.4
C8N2M1	109.8	99.8	113.2
N2M1N1	90.2	84.8	63.8
BAS[63]	647.3	626.4	622.9
Exocyclic bond angles, deg			
C7N1C3	122.5	121.5	127.2
C4N2C8	121.8	120.0	117.0
N4C5S3	123.9	124.8	126.3
C6C5S3	119.2	118.7	118.4
C6C4S2	123.5	123.9	124.0
N2C4S2	123.0	119.1	119.2
N1C3S4	119.1	119.0	118.3
C2C3S4	123.7	124.0	122.5
N3C1S1	124.1	124.2	127.4
C2C1S1	118.8	117.5	117.8
Torsion angles, deg			
N1M1N4C5	122.0	114.3	65.1
N2M1N3C1	113.8	10.3	90.1
N4M1N1C7	−136.6	−142.3	−88.0
N3M1N2C8	−44.9	−19.3	−7.8
M1N2C8O1	−64.3	−75.5	−102.0
M1N1C7O1	64.0	70.7	−57.3
N2C8O1C7	79.9	79.7	86.3
N1C7O1C8	−79.6	−74.6	−73.6
M1N4C5C6	1.6	−14.8	−13.4
M1N2C4C6	85.6	−48.0	−51.2
N4C5C6C4	−4.9	−44.5	−46.8
N2C4C6C5	−52.1	82.1	88.7
M1N3C1C2	1.0	−3.4	4.5
M1N1C3C2	80.6	77.4	112.5
N3C1C2C3	5.3	14.5	−24.6
N1C3C2C1	−58.2	−61.2	−90.7
M1N1C3S4	−98.6	−100.1	−67.4
M1N3C1S1	−179.2	178.5	−177.1
M1N4C5S3	179.9	165.2	165.3
M1N2C4S2	−97.8	124.8	122.8
S1C1C2C3	−174.6	−167.4	156.9
S2C4C6C5	131.4	−90.4	−84.9
S3C5C6C4	176.7	135.5	134.3
S4C3C2C1	121.0	116.1	89.2

Table 2. Standard enthalpies, entropies, and Gibbs energies of formation of isomeric asymmetric macrocyclic metal complexes **I** and **II**

Complex type	M(II)	$\Delta H^0_{f,298}$, kJ/mol	$S^0_{f,298}$, J mol/K	$\Delta G^0_{f,298}$, kJ/mol
I	Mn(II)	–	–	–
	Fe(II)	–	–	–
	Co(II)	–	–	–
	Ni(II)	–	–	–
	Cu(II)	–	–	–
	Zn(II)	–	–	–
II	Mn(II)	–	–	–
	Fe(II)	–	–	–
	Co(II)	–	–	–
	Ni(II)	296.8	759.6	280.3
	Cu(II)	398.0	746.7	386.4
	Zn(II)	198.2	727.2	194.9

The ground state of the Ni(II) complex is the spin triplet, i.e., it is a high-spin complex. Note that the energy difference between the triplet ground state and the nearest singlet state is small (only 6.9 kJ/mol); therefore, spin isomerism (spin crossover) for this complex is quite probable. For the Cu(II) and Zn(II) complexes, in full conformity with theoretical expectations, the ground states are spin doublet and singlet, respectively; the energy difference between the structures with the spin multiplicity other than the ground state multiplicity is rather large (165.4 and 204.0 kJ/mol, respectively).

The metal–nitrogen bond lengths are different in all of the considered complexes and only in the Ni(II) complex, the M1N3 and M1N4 bond lengths are similar (188.8 and 188.4 pm, respectively); on going from Ni to Zn, the M–N bond lengths generally increase.

The sums of interior (non-bond) angles in the N_4 group of donor atoms are much smaller than 360°, which implies some non-coplanarity of this group; this is especially pronounced for the Ni(II) complex where the deviation is more than 80° (Table 1). This complex, like the copper(II) complex, is characterized by the presudotetrahedral coordination of the ligand donor sites relative to the central atom M (the sum of bond angles in the MN_4 chelate unit is 408.2° and 367.4°, respectively). An interesting feature was noted for the Zn(II) complex: the nitrogen atom coordination to the complexing atom looks like quasi-pyramidal but the sum of bond angles N1M1N2, N2M1N4, N4M1N3, and N3M1N1 in the MN_4 chelate unit is 359.0°, which is close to the bond angle sum for a planar structure of this atomic group. By analogy with the (565)macrotricyclic complexes in most of which five-membered rings in the same complex differ both by the set of bond angles and by the sum of angles, one can expect that in the considered (666)macrotricyclic complexes, all of the three six-membered rings would also differ. Indeed, the sums of the interior bond angles in these rings are considerably different, the difference being most clear-cut in the Zn(II) complex with bond angle sums of 610.3°, 669.1°, and 622.9°. The deviation of the sum of bond (interior) angles in the first ring from the sum of interior angles of a planar hexagon (720°) is almost 110°, which is a sort of record-breaking non-coplanarity for six-membered rings in template metal macrocyclic compounds.

As regards the extracyclic bond angles outside the chelate rings, none of the complexes has a pair of equal angles; the same lack of equality is observed for bond lengths both inside and outside the chelate rings. The values of these parameters depend rather little on the nature of the M(II) complexing ion.

The nitrogen–hydrogen bond lengths also depend little on the nature of M(II) and differ insignificantly in the same complex (for example, the N1H9 bond length in the Cu(II) chelate is 102.1 pm, the N2H10 bond length is the 102.2 pm, and the N3H12 and N4H11 bond lengths are 101.9 pm each) (Table 1). Conversely, the torsion (dihedral) angles depend substantially on the nature of the complexing ion.

The standard enthalpies of formation ($\Delta H^0_{f,298}$) and the Gibbs energies of formation ($\Delta G^0_{f,298}$) for all metal complexes **II** we consider are positive and often fairly large (Table 2). The standard entropies of formation ($S^0_{f,298}$) of these compounds are also quite large (hundreds of J/mol K). This means that the complexes cannot be obtained from separate chemical elements and suggests that overall process (2) giving complexes **II** would most likely prove to be thermodynamically forbidden for being implemented in solution or in the solid phase. Perhaps, this is why the formation of these complexes under "traditional" conditions of complexation has not been observed as yet. However, under specific conditions, namely, in nanostructured organizing systems such as metal hexacyanoferrate(II) gelatin-immobilized matrix implants, the formation of complexes **II** was reported [2] to be still possible.

REFERENCES

1. D. V. Chachkov and O. V. Mikhailov, Russ. J. Inorg. Chem. **54**, 1952 (2009).
2. O. V. Mikhailov, Inorg. Chim. Acta **394**, 664 (2013).
3. O. V. Mikhailov, M. A. Kazymova, T. A. Shumilova, et al., Trans. Metal Chem .**28**, 592 (2003).
4. O. V. Mikhailov, M. A. Kazymova, and D. V. Chachkov, Russ. J. Inorg. Chem. **58**, 1518 (2013).

5. D. V. Chachkov and O. V. Mikhailov, Russ. J. Inorg. Chem. **58**, 1073 (2013).
6. D. V. Chachkov and O. V. Mikhailov, Russ. J. Inorg. Chem. **58**, 1203 (2013).
7. D. V. Chachkov and O. V. Mikhailov, Russ. J. Inorg. Chem. **58**, 1315 (2013).
8. O. V. Mikhailov, D. V. Chachkov, and O. N. Grigorieva, Inorg. Chim. Acta **408**, 199 (2013).
9. O. V. Mikhailov and D. V. Chachkov, Inorg. Chim. Acta **408**, 246 (2013).
10. O. V. Mikhailov, D. V. Chachkov, and O. N. Grigorieva, Central Eur. J. Chem. **11**, 1822 (2013).
11. A. Schaefer, H. Horn, and R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992).
12. A. Schaefer, C. Huber, and R. Ahlrichs, J. Chem. Phys. **100**, 5829 (1994).
13. W.-M. Hoe, A. Cohen, and N. C. Handy, Chem. Phys. Lett. **341**, 319 (2001).
14. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
15. H. Paulsen, L. Duelund, H. Winkler, et al., Inorg. Chem. **40**, 2201 (2001).
16. M. Swart, A. R. Groenhof, A. W. Ehlers, and K. Lammertsma, J. Phys. Chem. A **108**, 5479 (2004).
17. M. Swart, A. W. Ehlers, and K. Lammertsma, Mol. Phys. **102**, 2467 (2004).
18. M. Swart, Inorg. Chim. Acta **360**, 179 (2007).
19. M. J. Frisch et al., Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT, 2009.
20. J. Tomasi, B. Mennucci, and E. Cancès, J. Mol. Struct. (Theochem) **211**, 464 (1999).
21. D. V. Chachkov and O. V. Mikhailov, Russ. J. Inorg. Chem. **56**, 223 (2011).
22. D. V. Chachkov, O. V. Mikhailov, and M. N. Astaf'ev, Zh. Strukt. Khim. **50**, 645 (2009).
23. O. V. Mikhailov and D. V. Chachkov, Russ. J. Gen. Chem. **83**, 1123 (2013).

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