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Molecular Structure of $M(N_{13})$ Compounds with 12-Membered Nitrogen-Containing Cycle and Axial Nitrogen Atom (M = Mn, Fe): Quantum-Chemical Design by DFT Method

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Abstract: Based on the results of a quantum chemical calculation using the DFT method in the B3PW91/TZVP, OPBE/TZVP, M06/TZVP, and M062/Def2TZVP levels, the possibility of the existence of $M(N_{13})$ chemical compounds (M = Mn, Fe) that are unknown for these elements has been predicted. Data on the structural parameters, the multiplicity of the ground state, APT and NBO analysis, and standard thermodynamic parameters of formation (standard enthalpy $\Delta_f H^0$, entropy S^0, and Gibbs's energy $\Delta_f G^0$) for these compounds are presented.

Keywords: $M(N_{13})$; manganese; iron; molecular structure; DFT method

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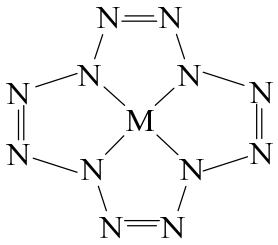
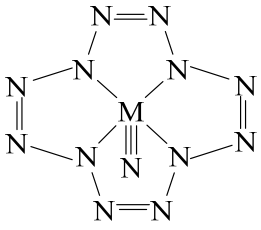
1. Introduction

One of the very interesting problems of modern inorganic chemistry is the problem of stabilization of polynuclear structures consisting only of nitrogen atoms, and in particular, of various polynitrogens. Among the possible ways to solve this problem is the stabilization of these structures through their "metallization", the meaning of which is the formation of chemical bonds by nitrogen atoms with atoms of various metals, primarily with atoms of *d*-elements. In our previous article [1], a quantum-chemical calculation of the molecular and electronic structures of *3d*-element (M) compounds with nitrogen, having a structural formula (I) (see Figure 1) with a ratio between the number of atoms M and nitrogen equal to 1:12, where M = Ti, V, Cr, Mn, Fe, Co, Ni, or Cu, was carried out, and the fundamental possibility of their existence was shown using quantum-chemical methods DFT B3PW91/TZVP, M06/TZVP, OPBE/TZVP, and MP2/TZVP for each of the above *d*-elements. Due to the formation of such a structure with the participation of the central atom of the *3d* element, stabilization of the structural fragment of twelve nitrogen atoms takes place, which, according to the data presented in [2–10], if capable of existing as a separate molecule, is very unstable. In this regard, it seems interesting to find out whether, in principle, the existence of chemical compounds of general formula (II) (Figure 2) is possible, which, like the compounds described in [1], contain a 12-membered cycle of nitrogen atoms and a nitride anion in an axial position relative to the group of the four nitrogen atoms bonded to the M atom in a total of seven covalent bonds, as follows:



(I)

Figure 1. The structure of $M(N_{12})$ compound described in [1].



(II)

Figure 2. The structure of $M(N_{13})$ compound.

Taking into account the number of valence electrons in the 4*s* and 3*d* orbitals and the valence capabilities of the M atoms of the 3*d* elements, it can be expected that compounds with the structural formula II can form a few of these M, namely, only those that have seven or more in the above orbitals more electrons. Although there are six such elements (Mn, Fe, Co, Ni, Cu, and Zn), one can actually expect their formation only for two of them, namely Mn and Fe, for which compounds are known where these elements form seven covalent bonds with other atoms (namely, $KMnO_4$ and $KFeO_4$). Be that as it may, there is no information about the compounds of formula II in the literature, although a number of publications have considered two-element chemicals containing atoms of *s*-, *p*- or *d*-elements and nitrogen atoms (see, in particular, [11–16]). It should be noted that almost every one of these works mentioned the possible use of such compounds as potential high-energy materials. A discussion of the possibility of the existence of type II compounds for various M of 3*d* elements, as well as the dependence of the parameters of their molecular and electronic structure on the nature of M, is the subject of this article.

2. Method

In this work, we used the density functional theory (DFT), which combines the standard extended split-valence basis set TZVP and the most modern hybrid functional M06, described in detail in [17]. For comparison, the other version of the DFT method, namely DFT with B3PW91 functional, is described in detail in Refs. [18–20] and used by us in [21–23]. The use of the given version of the DFT method, in this case, is because, according to [18–20], it allows one to obtain, as a rule, the most accurate (i.e., close to experimental) values of the geometric parameters of molecular structures, as well as much more accurate values of thermodynamic and other physical–chemical parameters in comparison with other variants of the DFT method. In addition to them, we also calculated the molecular and electronic structures of these compounds using the DFT OPBE/TZVP method, which combines the above TZVP basis and the non-hybrid OPBE functional [24,25], which, according to the data of works [25–29], in the case of compounds of 3*d*-elements, gives a fairly accurate ratio of the energy stability of the high-spin state with respect to the low-spin state and, at the same time, reliably characterizes the key geometric parameters of the molecular structures of the metal compounds under consideration. We also used two other versions of the DFT method, the functionals of which are most adequate for describing the parameters of the molecular and electronic structures of *d*-elements, namely, DFT M06/TZVP and DFT M062X/Def2TZVP, the details of which are described in [17]. The calculations were carried out using the Gaussian09 program package [30]. As in our previous articles, in which this method of calculation was used [21–23], the correspondence of the found stationary points

to the energy minima in all cases was proved by calculating the second derivatives of the energy to the coordinates of the atoms, wherein all equilibrium structures corresponding to the minimum points on the potential energy surfaces had only real (and, moreover, always positive) frequency values. Of the optimized structures for further consideration, the one with the lowest total energy was selected. Unfortunately, at the moment, in our studies, we had to limit ourselves to calculations using various versions of the DFT method, since for the compounds we are considering, when completing the calculation with any of the higher-level methods (QCISD, CCSD, and even MP2), due to the complexity of these methods and our limited time and energy costs, we failed. Atomic polar tensors (APT) analysis was carried out using APT version 3.1 integrated with the Gaussian09 program package [30] according to the methodology described in detail in [31]. The APT method is well-known for excellent numerical stability and convergence with respect to basis set expansion and is sensibly proportionate to the convergence of energy and other calculated wavefunction properties (unlike Mulliken analysis and related overlap-dependent methods). For comparison, NBO analysis, which was carried out according to [32], was also used. The standard thermodynamic parameters of formation ($\Delta_f H^0$, S^0, and $\Delta_f G^0$) for the M(N_{13}) compounds under examination were calculated according to the methodology described in [33].

3. Results and Discussion

According to the data of each of the above three versions of the DFT calculation, compounds of the M(N_{13}) type having molecular structures (II) can exist only for two 3*d* elements, namely for Mn and Fe, as we assumed above. The interatomic distances of M—"axial" nitrogen atoms for these M, depending on the calculation method, is in the range of 150.0–152.5 pm, which is significantly (by more than 30 pm) shorter than the bond lengths of M—"equatorial" nitrogen atoms; this may serve as an indication that the chemical bond formed between them is not single or even double, but triple. In this regard, it should be noted that in the case of 3*d* elements following Fe in Mendeleev's Periodic System (i.e., Co, Ni, Cu, and Zn), on the one hand, the interatomic distances of M—"axial" nitrogen atoms (in the framework of the OPBE/TZVP method for M = Co, 155.3; M = Ni, 166.9; M = Cu, 186.1; M = Zn, 194 pm), on the other hand, the difference between these distances and the bond lengths of M—"equatorial" nitrogen atoms (which are equal to 181.1, 186.2, 188.3, and 209.4 pm, respectively) is much smaller, since the formation of a triple bond in the case of each of these four M becomes very doubtful. In view of this important circumstance, in what follows, we will only discuss two type II compounds, namely, Mn(N_{13}) and Fe(N_{13}). The most important geometric parameters of the molecular structures of these compounds (the lengths of chemical bonds between atoms and bond angles) obtained within the framework of each of the variants of the DFT method used by us are presented in Table 1. As follows from the data presented in it, a grouping of four nitrogen atoms bound with the M atom by single bonds, in both of the above compounds of M(N_{13}), is strictly flat, because the sum of the angles N1N4N7, N4N7N10, N7N10N1, and N10N1N4 in each of them is 360.0°, and this takes place within each of the three variants of the method used in the work DFT. There is, however, a small nuance. In the case of Mn(N_{13}) within the framework of the DFT B3PW91/TZVP, DFT OPBE/TZVP, and DFT M062X/Def2TZVP methods, all the above non-bonding angles are equal to each other and amount to 90°, while according to the data from DFT M06/TZVP, they are equal only in pairs, although the deviation of their values from 90° is smaller than 0.5°. However, in the case of Fe(N_{13}), within the framework of the DFT B3PW91/TZVP and DFT OPBE/TZVP methods, all the above non-bonding angles are equal to each other and amount to 90°, while according to the data of the DFT M06/TZVP and DFT M062X/Def2TZVP methods, they are equal only in pairs, but the deviation of their values from 90° exceeds 0.5° (Table 1). Both in the case of Mn(N_{13}) and in the case of Fe(N_{13}), the N4 group has the shape of either a square (within the DFT B3PW91/TZVP and DFT OPBE/TZVP methods) or a parallelogram (within the DFT M06/TZVP and DFT M062X/Def2TZVP methods). However, the

grouping of MN4 atoms in both of these chemical compounds has a tetragonal-pyramidal structure with a very significant (more than 45°) deviation from the plane formed by four "equatorial" nitrogen atoms bonded to the M atom (Table 1). This deviation somewhat depends on the DFT method used in the calculation, but it is always more pronounced for $Mn(N_{13})$, which is quite natural if we take into account the somewhat larger radius of the Mn atom compared to the radius of the Fe atom. Thus, in both $M(N_{13})$ compounds, the M atom is to some extent elevated above the plane of the four "equatorial" nitrogen atoms. Within the framework of the DFT B3PW91/TZVP and DFT OPBE/TZVP methods, the lengths of the four M–N bonds in both compounds under consideration are the same; within the framework of the DFT M06/TZVP and DFT M062X/Def2TZVP methods, they are different, although not too strongly (Table 1). The 12-membered macrocycles formed by nitrogen atoms in each of these two compounds are also non-coplanar, which is clearly seen even from the images of their molecular structures, presented in Figure 3. The values of the electrical dipole moments (μ) of these compounds, as expected, are quite noticeably different from 0 and are 1.66 and 1.70 in the DFT B3PW91/TZVP method and 1.77 and 1.79 Debye units in the DFT M06/TZVP method. Calculation by the DFT OPBE/TZVP method gives significantly lower values of this parameter; moreover, interestingly, for both of these compounds, it turns out to be almost the same, namely, 1.27 Debye units.

Table 1. Key parameters of molecular structures of $Mn(N_{13})$ and $Fe(N_{13})$ compounds calculated by DFT B3PW91/TZVP, OPBE/TZVP, M06/TZVP, and M062X/Def2TZVP levels.

	$Mn(N_{13})$				**$Fe(N_{13})$**			
Structural Parameter	**B3PW91/ TZVP**	**OPBE/ TZVP**	**M06/ TZVP**	**M062X/ Def2TZVP**	**B3PW91/ TZVP**	**OPBE/ TZVP**	**M06/ TZVP**	**M062X/ Def2TZVP**
M–N bond lengths in the MN_4 chelate node, *pm*								
M1N1	188.4	188.5	190.7	191.1	183.0	182.6	184.5	184.9
M1N4	188.4	188.5	189.3	191.1	183.0	182.6	183.1	188.8
M1N7	188.4	188.5	189.3	191.1	183.0	182.6	183.1	188.8
M1N10	188.4	188.5	190.7	191.1	183.0	182.6	184.5	184.9
M–N bond lengths between M and nitride N atom, *pm*								
M1N13	151.0	152.5	150.9	147.3	150.9	151.5	150.0	154.4
Nitrogen-nitrogen bond lengths in macrocycle, *pm*								
N1N2	134.9	134.9	138.4	142.1	134.5	134.9	138.8	136.2
N2N3	127.2	128.2	125.9	123.4	127.5	128.2	125.8	123.8
N3N4	134.9	134.9	134.0	142.1	134.5	134.9	134.0	142.9
N4N5	134.9	134.9	137.6	129.9	134.5	134.9	137.6	130.0
N5N6	127.2	128.2	124.6	132.3	127.5	128.2	124.6	131.3
N6N7	134.9	134.9	137.6	130.0	134.5	134.9	137.6	130.0
N7N8	134.9	134.9	134.0	142.1	134.5	134.9	134.0	142.9
N8N9	127.2	128.2	125.9	123.4	127.5	128.2	125.8	123.8
N9N10	134.9	134.9	138.4	142.1	134.5	134.9	138.8	136.2
N10N11	134.9	134.9	132.0	129.9	134.5	134.9	131.4	137.9
N11N12	127.2	128.2	129.4	132.3	127.5	128.2	129.9	124.2
N12N1	134.9	134.9	132.0	130.0	134.5	134.9	131.4	137.9

Table 1. *Cont.*

Structural Parameter	Mn(N_{13})				Fe(N_{13})			
	B3PW91/ TZVP	**OPBE/ TZVP**	**M06/ TZVP**	**M062X/ Def2TZVP**	**B3PW91/ TZVP**	**OPBE/ TZVP**	**M06/ TZVP**	**M062X/ Def2TZVP**
Bond angles in the MN_4 grouping, *deg*								
N1M1N4	76.3	76.0	76.0	74.6	77.7	77.7	77.4	76.2
N4M1N7	76.3	76.0	75.7	75.6	77.7	77.7	77.1	78.0
N7M1N10	76.3	76.0	76.0	74.6	77.7	77.7	77.4	76.2
N10M1N1	76.3	76.0	76.3	75.6	77.7	77.7	78.0	76.0
Bond angles sum (***BAS***), *deg*	305.2	304.0	304.0	300.4	310.8	310.8	309.9	306.4
Deviation from coplanarity, *deg*	54.8	56.0	56.0	59.6	49.2	49.2	50.1	53.6
Non-bond angles in the MN_4 grouping, *deg*								
N1N4N7	90.0	90.0	90.4	90.0	90.0	90.0	90.5	88.8
N4N7N10	90.0	90.0	90.4	90.0	90.0	90.0	90.5	88.8
N7N10N1	90.0	90.0	89.6	90.0	90.0	90.0	89.5	91.2
N10N1N4	90.0	90.0	89.6	90.0	90.0	90.0	89.5	91.2
Non-bond angles sum (NBAS), *deg*	360.0	360.0	360.0	360.0	360.0	360.0	360.0	360.0
Deviation from coplanarity, *deg*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bond angles in 5-membered cycles, *deg*								
M1N1N2	117.8	118.2	117.4	117.7	117.8	118.1	117.4	119.1
N1N2N3	113.1	112.6	111.3	112.4	112.3	112.0	110.4	114.9
N2N3N4	113.0	112.6	115.4	112.4	112.3	112.0	114.5	110.1
N3N4M1	117.8	118.2	118.0	117.7	117.8	118.1	118.2	116.9
M1N4N5	117.8	118.2	118.0	119.1	117.8	118.1	118.3	116.9
N4N5N6	113.0	112.6	113.0	113.1	112.3	112.0	112.1	114.1
N5N6N7	113.1	112.6	113.0	113.1	112.3	112.0	112.1	114.1
N6N7M1	117.8	118.2	118.0	119.1	117.8	118.1	118.3	116.9
M1N7N8	117.8	118.2	118.0	117.7	117.8	118.1	118.2	116.8
N7N8N9	113.1	112.6	115.4	112.4	112.3	112.0	114.5	110.1
N8N9N10	113.0	112.6	111.3	112.4	112.3	112.0	110.4	114.9
N9N10M1	117.8	118.2	117.4	117.7	117.8	118.1	117.4	119.1
M1N10N11	117.8	118.2	117.7	119.1	117.8	118.1	117.7	119.1
N10N11N12	113.0	112.6	113.7	113.1	112.3	112.0	112.9	112.0
N11N12N1	113.1	112.6	113.7	113.1	112.3	112.0	112.9	112.0
N12N1M1	117.8	118.2	117.7	119.1	117.8	118.1	117.7	119.1
N–M–N bond lengths between N donor atom, M, and nitride N atom, *pm*								
N1M1N13	119.1	119.5	120.4	120.5	117.4	117.4	117.3	124.0
N4M1N13	119.1	119.5	118.5	120.5	117.4	117.4	118.1	113.5
N7M1N13	119.1	119.5	118.5	120.5	117.4	117.4	118.1	113.5
N10M1N13	119.1	119.5	120.4	120.5	117.4	117.4	117.3	124.0

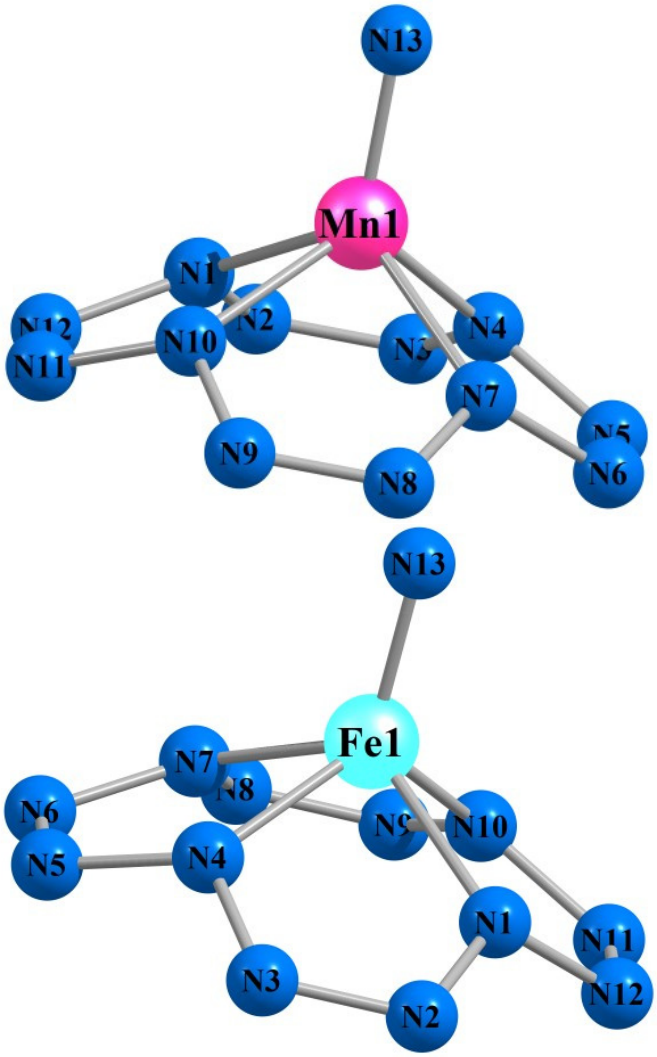


Figure 3. Molecular structures of the $Mn(N_{13})$ and $Fe(N_{13})$ compounds obtained as a result of DFT B3PW91/TZVP quantum-chemical calculation.

APT and NBO analysis data for the compounds under study obtained by DFT M062X/Def2TZVP level are presented in Table 2; similar data obtained by DFT B3PW91/TZVP, DFT OPBE/TZVP, and DFT M06/TZVP can be found in the Supplementary Materials. As can be seen from these data, the values of the effective charges on the M and N atoms are quite different from those that might be expected if all the compounds present in the compounds under consideration were purely ionic; this circumstance indicates a very pronounced delocalization of the electron density within the entire molecular structure of $M(N_{13})$. Characteristically, the effective charges on the M atoms in the framework of the APT analysis are positive (although very small in absolute value), while in the framework of the NBO analysis, they are negative in the case of $Mn(N_{13})$ and positive in the case of $Fe(N_{13})$ (Table 2). On the whole, a similar situation occurs in the case of the other three DFT methods (see the Supplementary Materials). Taking into account the important fact that the electronegativity of the nitrogen atom is much greater than the electronegativity of the iron and manganese atoms, the effective charges on the atoms presented in Table 2 look rather unusual; the question of how much they correspond to reality is still open to us.

Table 2. APT and NBO analysis data for Mn(N_{13}) and Fe(N_{13}) according to DFT M062X/Def2TZVP.

APT Analysis Data								
M	Effective charge on an atom, units electron charge ē							
	M1	N1 (N10)	N2 (N9)	N5 (N6)	N4 (N7)	N3 (N8)	N11(N12)	N13
Mn	+0.377	−0.151 (−0.151)	+0.079 (+0.079)	+0.025 (+0.024)	−0.151 (−0.151)	+0.079 (+0.079)	+0.025 (+0.024)	−0.185
Fe	+0.115	−0.209 (−0.209)	+0.131 (+0.131)	−0.014 (−0.014)	−0.050 (−0.050)	−0.050 (−0.050)	+0.029 (+0.029)	+0.211
NBO Analysis Data								
M	Effective charge on an atom, units electron charge ē							
	M1	N1 (N10)	N2 (N9)	N5 (N6)	N4 (N7)	N3 (N8)	N11(N12)	N13
Mn	−0.065	−0.113 (−0.113)	+0.057 (+0.057)	+0.012 (+0.012)	−0.113 (−0.113)	+0.057 (+0.057)	+0.012 (+0.012)	+0.239
Fe	+0.056	−0.167 (−0.167)	+0.075 (+0.075)	+0.023 (+0.023)	−0.040 (−0.040)	+0.004 (+0.004)	+0.021 (+0.021)	+0.111

According to the data of each of these three methods, the ground state of Mn(N_{13}) is a spin triplet, which is in good agreement with the values of the squared intrinsic angular momentum of the total spin <S**2>, equal to 2.0016 (in the case of the DFT B3PW91/TZVP), 2.0009 (in the case of DFT OPBE/TZVP), 2.0209 (in the case of DFT M06/TZVP), and 2.0264 (in the case of DFT M062/Def2TZVP). The Fe(N_{13}) ground state is a spin doublet, which also corresponds to the <S**2> values for this spin multiplicity (0.7508 (DFT B3PW91/TZVP), 0.7501 (DFT OPBE/TZVP), 0.7537 (DFT M06/TZVP), and 1.4530 (M062/Def2TZVP)). As can be seen from these data, for both studied compounds, the three variants of the DFT method used by us give <S**2> values that are very close to each other, although their functionals differ quite significantly from each other. However, if in the case of Fe(N_{13}), the multiplicity of the ground state (which corresponds to the presence of one unpaired electron) seems quite natural, since the Fe atom is bound to nitrogen atoms by seven bonds and its electronic configuration in this compound can be $3d^1$, then in the case of Mn(N_{13}), the triplet ground state looks somewhat unexpected, since in this case, with the same number of metal–nitrogen bonds as in Fe(N_{13}), its electronic configuration should be $3p^5 4s^1$ (but not $3p^6$, which seems a priori more probable). In this regard, it is worth noting that the nearest excited state for Mn(N_{13}), according to the data of each of these three DFT methods, is a spin singlet whose energy shows 23.3 (DFT B3PW91/TZVP), 12.8 kJ/mol (DFT OPBE/TZVP), and 39.6 (DFT M062X/Def2TZVP) more ground state energy. A similar situation also occurs in the case of Fe(N_{13}), where, according to the data of each of these methods, the nearest excited state is a spin quartet whose energy exceeds the energy of the ground state by 160.6, 190.1, and 174.0 kJ/mol, respectively. Images of the highest occupied and lowest vacant molecular orbitals (HOMO and LUMO, respectively) for the compounds under consideration, obtained by each of these three DFT methods above, are presented in Figures 4 and 5.

The standard thermodynamic parameters of formation for the compounds under examination ($\Delta_f H^0$, S^0, and $\Delta_f G^0$) are presented in Table 3. As can be seen from it, each of these parameters is positive. According to canons of thermodynamics, none of them can be obtained from the simple substances formed by chemical elements in their compositions (i.e., N and corresponding M). Nevertheless, according to the data obtained as a result of the quantum-chemical calculation carried out by us, the molecular structures of the given compounds and the full totality of their geometric parameters can be realized as a single whole. Thus, it can be argued that they are capable of existence, at least in the gas phase as individual molecules. It should be noted that, according to data of each of the DFT methods indicated above, $\Delta_f H^0$ and $\Delta_f G^0$ values for Fe(N_{13}) are greater than

for Mn(N_{13}), whereas, for S^0 values, an inverse ratio takes place (Table 2). It should be noted that the calculation of $\Delta_f H^0$, S^0, and $\Delta_f G^0$ parameters using DFT M062/Def2TZVP was considered inappropriate by us, because M062X is a global hybrid functional with 54% HF exchange, and it is the top performer within the 06 functionals for main group thermochemistry, kinetics, and non-covalent interactions; however, it cannot be used for cases where multi-reference species are or might be involved, such as in transition metal thermochemistry and organometallics [34]).

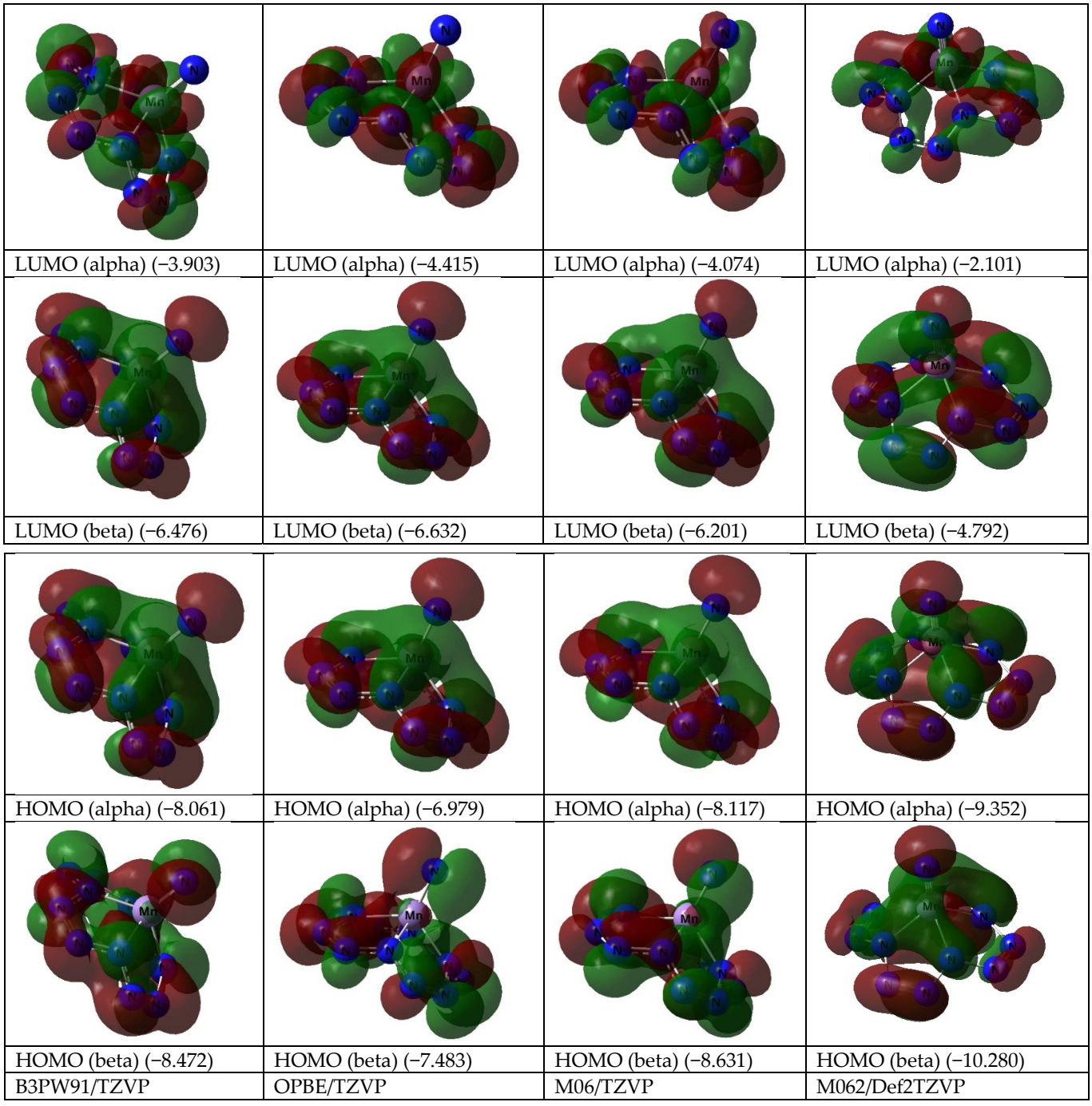


Figure 4. The pictures of HOMO and LUMO in the Mn(N_{13}) obtained according to the DFT D3PW91/TZVP, DFT OPBE/TZVP, DFT M06/TZVP, and DFT M062/Def2TZVP methods. The energy values of the given MOs (in brackets) are expressed in eV.

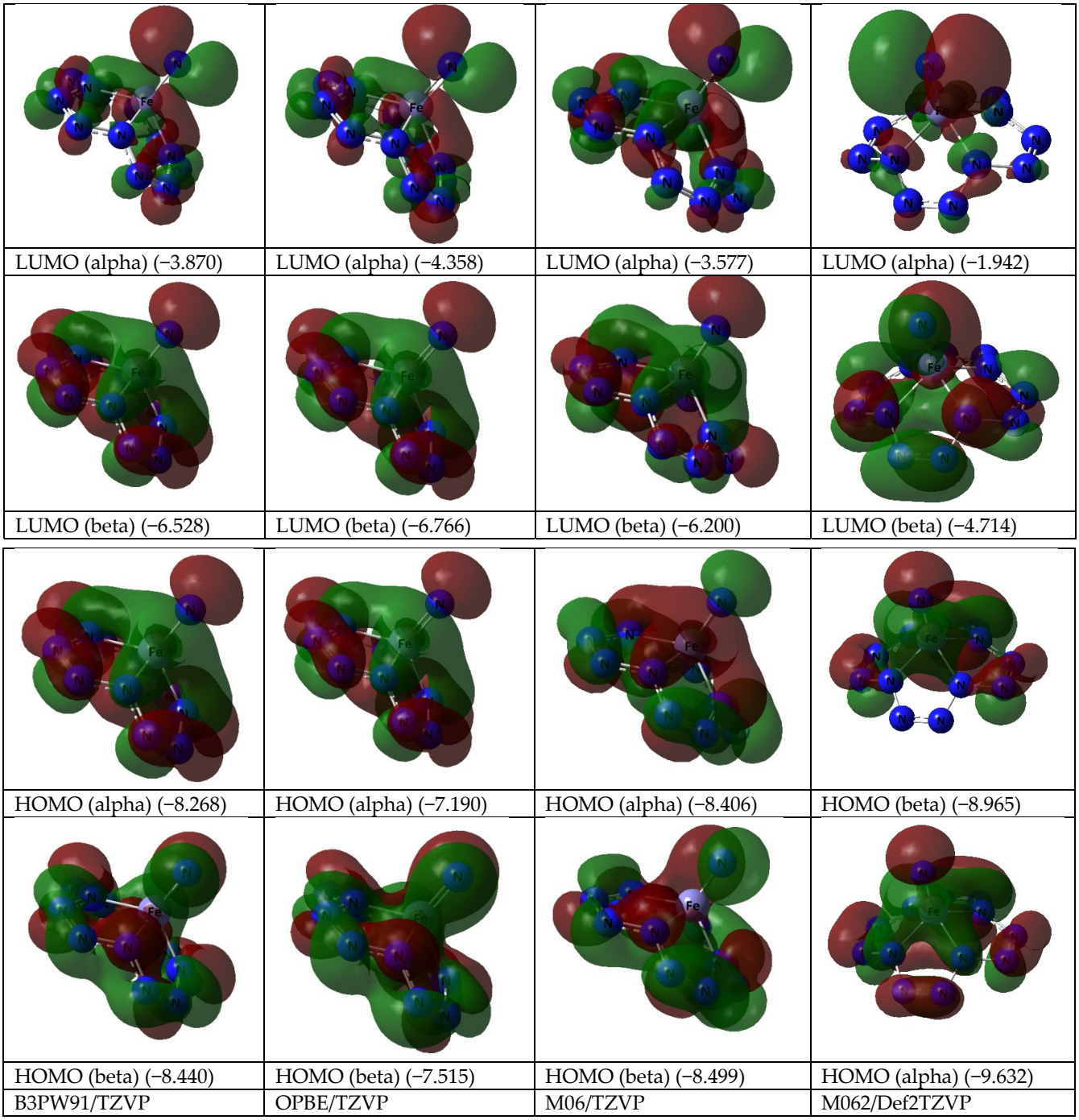


Figure 5. The pictures of HOMO and LUMO in the Fe(N_{13}) obtained according to the DFT D3PW91/TZVP, DFT OPBE/TZVP, DFT M06/TZVP, and DFT M062/Def2TZVP method. The energy values of the given MOs (in brackets) are expressed in eV.

In conclusion of this section, it seems appropriate to compare the key data of the Mn(N_{13}) and Fe(N_{13}) compounds studied by us in this work with similar data of the Mn(N_{12}) and Fe(N_{12}) compounds close to them in composition, which were presented in our work [1] and its Supplementary Materials and also calculated with DFT B3PW91/TZVP, DFT M06/TZVP, and DFT OPBE/TZVP. A comparison of these data shows that the key fragment of the M(N_{13}) molecular structure, namely, the N12 macrocycle, as a whole, does not undergo noticeable changes compared to that in the M(N_{12}) molecular structure. What has just been said also applies to the degree of deviation of the MN4 groupings from coplanarity, which in M(N_{13}), for any of the two M we considered, and in the framework of

any of the three variants of the DFT method used in the calculation, is only slightly greater than in the corresponding compound $M(N_{12})$ (in particular, within the framework of the DFT B3PW91/TZVP method, in the case of $Fe(N_{13})$, it is 49.2°, while in the case of $Fe(N_{12})$, it is 47.1°). This slight change can be attributed to the fact that the formation of a rather short triple bond by the M atom with the "axial" nitrogen atom should additionally "raise" the M atom above the plane of the four N atoms that form chemical bonds with it.

Table 3. Standard thermodynamic parameters of $Mn(N_{13})$ and $Fe(N_{13})$ calculated by various methods.

Compound	Calculation Method	$\Delta_f H^0$, kJ/mol	S^0, J/mol·K	$\Delta_f G^0$, kJ/mol
$Mn(N_{13})$	DFT B3PW91/TZVP	1704.9	424.4	1956.4
	DFT OPBE/TZVP	1411.2	429.5	1661.2
	DFT M06/TZVP	1834.5	425.7	2085.6
$Fe(N_{13})$	DFT B3PW91/TZVP	1821.2	422.7	2071.8
	DFT OPBE/TZVP	1486.3	416.8	1738.6
	DFT M06/TZVP	1980.1	419.8	2231.6

4. Conclusions

The above data, obtained using three variants of the DFT method with different functionals, namely DFT B3PW91/TZVP, DFT M06/TZVP, and DFT OPBE/TZVP, unambiguously predict the possibility of the existence of new, hitherto unknown chemical compounds, $Mn(N_{13})$ and $Fe(N_{13})$, containing a cyclic group of twelve nitrogen atoms and an "axial" N atom bonded to the Mn or Fe atom via a triple bond. At the same time, each of these three methods testifies to the impossibility of the existence of compounds of the $M(N_{13})$ type for all other 3*d* elements. The results of calculating the molecular structure of both these compounds, obtained by the above variants of the DFT method, are in good agreement with each other not only qualitatively, but also quantitatively. Both of these compounds have a tetragonal-pyramidal structure of the MN4 group (M = Mn, Fe) with a very significant (more than 45°) deviation from coplanarity; however, the grouping of four N4 nitrogen atoms bonded to the M atom in any of these compounds is strictly planar. However, the 12-membered macrocycles formed by nitrogen atoms in both $Mn(N_{13})$ and $Fe(N_{13})$ are non-coplanar, with very significant deviations from coplanarity. Comparison of the calculation data for the parameters of molecular structures and the standard thermodynamic parameters of the $M(N_{13})$ (M = Mn, Fe) compounds we considered with the analogous parameters of the $M(N_{12})$ compounds of the same 3*d* elements, characterized in our previous article [1], allows us to note quite a significant similarity between them.

As it seems to us, the results of quantum chemical calculations within the framework of each of these three methods give every reason for a more thorough study of both of these chemical compounds, for which, first of all, it is necessary to experimentally confirm their existence. This has a direct meaning, if only because they are high-energy substances (since both of them, according to our calculation of $\Delta_f H^0$ and $\Delta_f H^0$ values, as a rule, are 1500 kJ/mol or more, depending on the DFT method used), and if successful in obtaining them, they will undoubtedly find some practical application, at least in the capacity indicated.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/quantum5010019/s1, $Mn(N_{13})$ calculation by B3PW91/TZVP method; $Mn(N_{13})$ calculation by M06/TZVP method; $Mn(N_{13})$ calculation by OPBE/TZVP method; $Mn(N_{13})$ calculation by M062X/Def2TZVP method; $Fe(N_{13})$ calculation by B3PW91/TZVP method; $Fe(N_{13})$ calculation by M06/TZVP method; $Fe(N_{13})$ calculation by OPBE/TZVP method; $Fe(N_{13})$ calculation by M062X/Def2TZVP method.

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