Spin state relaxation of iron complexes: The case for OPBE and S12g

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Abstract: The structures of nine iron complexes that show a diversity of experimentally observed spin ground states were optimized and analyzed using the Density Functional Theory (DFT). An extensive validation study of the new S12g functional was performed, with a discussion concerning the influence of the environment, geometry and its overall performance based on a comparison with the well-proven OPBE functional. The OPBE and S12g functionals gave the correct spin ground state for all investigated iron complexes. Since S12g performs remarkably well, it could be considered a reliable tool for studying the energetics of the spin state in complicated transition metal systems.

Keywords: density functional theory; Fe(II) and Fe(III) coordination compounds; validation study; spin states.

INTRODUCTION

Spin is an intrinsic and inherent property of atoms and molecules.[1] Most transition metal ions with partially filled d-shells can exhibit different kinds of spin multiplicity in the ground state, *i.e.*, can lead to different spin states. Depending on the oxidation number, iron complexes usually have either 5 or 6 d-electrons that can be distributed in an octahedral environment in at least two different ways: with a maximum number of unpaired electrons, leading to the high spin (HS) state, or with maximally paired electrons – giving the low spin (LS) state. Other possibilities of the distribution of electrons represent an intermediate (IS) spin state. Since HS, IS and LS complexes usually display quite different

structural, spectral and magnetic properties, and often reactivity, it is of the utmost importance to have both experimental and theoretical methods to determine correctly the spin ground state of a system. However, both experiment and theory have difficulties and problems, and many studies have been devoted to this issue in the last decade.[2–5]

From a broad palette of quantum mechanical methods, the density functional theory (DFT)[6–8] has emerged into the mainstream, mainly because it gives a good compromise between accuracy of the results and computational efficiency.[9–11] However, although the DFT, in principle, gives an exact energy, a universal functional is still unknown, leading to density functional approximations (DFAs). These DFAs are parameterized for different properties and, noteworthy, spin-state energies were not included in the development for most of nowadays available DFAs.[12] It has been shown that the accuracy of the results not only strongly depends on the choice of the DFAs, but also on the basis set that is used.[1,3,13,14] Early pure functionals, such as LDA,[15–17] BP86,[18,19] BLYP,[19,20] and PW91,[21,22] have a tendency to favor LS states,[14] while hybrid functionals, such as B3LYP,[23,24] PBE0[25] and M06,[26,27] systematically favor HS states.[14] For the reliable prediction of the correct spin ground state from a number of close lying states, OPBE[14] has emerged to be one of the best functionals for the task.[28] Recently, Swart constructed a new density functional that combines the best of OPBE (spin states, reaction barriers) with the best of PBE (weak interactions) into the S12g[5] DFA.

Previously, the relative spin state energies of seven iron complexes (**1–7**, Fig. 1) on OLYP[20,29] optimized geometries (**1–3**) and on crystal structures (**4–7**) with a variety of DFAs were reported, which already showed the good performance of OPBE for vertical spin state splittings.[14]

Herein, a detailed DFT study on OPBE optimized geometries of iron complexes (**1–7**) with experimentally established spin ground states, ranging from singlet to sextet, is reported together with an extension to include two iron porphyrinato complexes (**8** and **9**, Fig. 1) that were reported to have different electronic ground states in spite of their similarity.[30–32]

Furthermore, a comprehensive validation study of the S12g DFA,[5] together with an examination of the influence of the chemical environment, was performed on all the investigated complexes.

METHODOLOGY

All DFT calculations were performed with the Amsterdam Density Functional (ADF) suite of program.[33,34] MOs were expanded in an uncontracted set of Slater type orbitals (STOs) of triple-ζ quality containing diffuse functions (TZP)[35] and one set of polarization functions. Core electrons (1s for 2nd period and 1s2s2p for 3rd–4th period) were not treated explicitly during the geometry optimizations (frozen core approximation), as the core was shown to have a negligible effect on the obtained geometries.[36] An auxiliary set of s, p, d, f,

and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each self-consistent field (SCF) cycle.
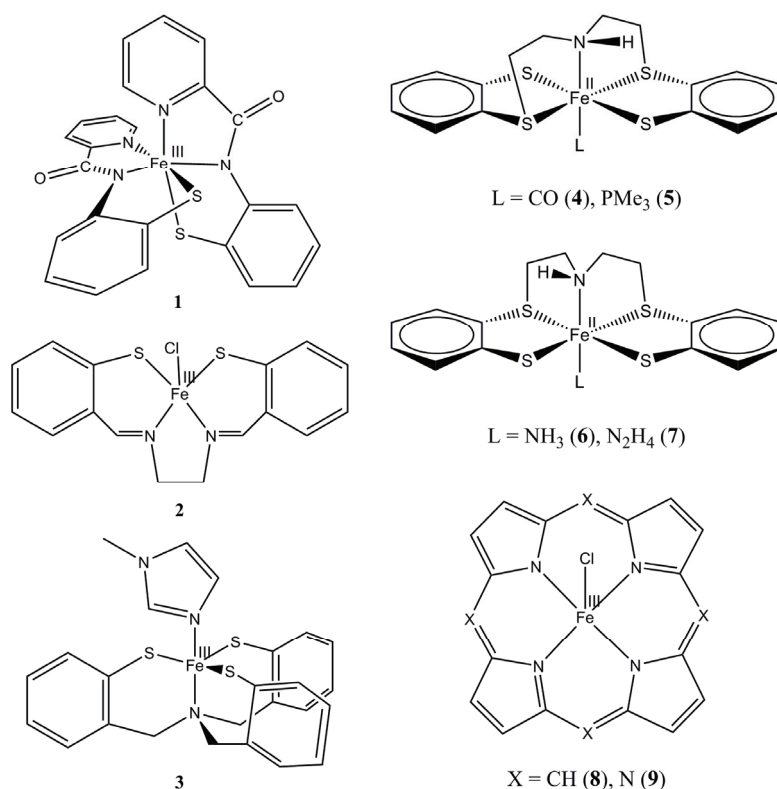

Fig. 1. Fe(PyPepS)$_2$ **1** (PyPepSH$_2$ = *N*-(2-mercaptophenyl)-2′-pyridinecarboxamide); Fe(tsalen)Cl **2** (tsalen = 2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[benzenethiolato]; Fe(N(CH$_2$-*o*-C$_6$H$_4$S)$_3$)(1-Me-imidazole) **3**; (Fe(NH)S$_4$)L **4** (L=CO), **5** (PMe$_3$), **6** (NH$_3$), **7** (N$_2$H$_4$)((NH)S$_4$ = bis(2-((2-mercaptophenyl)thio)ethyl)amine); iron porphyrin chloride (**8**, FePCl) and iron porphyrazine chloride (**9**, FePzCl).

Energies and gradients were calculated using the OPBE and S12g functionals in the gas phase and with COSMO (methanol as a solvent)[37-39] in the dielectric continuum model for a solvent environment. The geometries were optimized with the QUILD program[40] using adapted delocalized coordinates[41] until the maximum gradient component was less than 10^{-4} a.u. Subsequent single point calculations that utilize all electron basis set were performed on all optimized geometries, with OPBE and S12g.

RESULTS AND DISCUSSION

The total set of molecules consists of both Fe(III) (**1**–**3**, **8** and **9**) and Fe(II) (**4**–**7**) complexes, and show a diversity of experimentally observed spin ground states. A thorough examination with the OPBE and S12g functionals in the gas phase and the COSMO solvent environment was performed. The discussion is

commenced by focusing on the influence of structure relaxation on the spin states of Fe(III)-complexes **1**–**3**.[42] Experimentally, Fe-(PyPepS)$_2$ (**1**, PyPepSH$_2$ = *N*-(2--mercaptophenyl)-2-pyridinecarboxamide) has a LS doublet ground state,[43] Fe(tsalen)Cl (**2**, tsalen = 2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[benzenethiolato] 2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[benzenethiolato]) an intermediate spin (IS), quartet ground state[44] and Fe(N(CH$_2$-*o*-C$_6$H$_4$S)$_3$)(1-Me-imidazole, **3**) a HS sextet ground state.[45] Then, the Fe(II)-complexes ((Fe(NH)S$_4$)L, (NH)S$_4$ = bis(2-((2-mercaptophenyl)thio)ethyl)amine, L = CO (**4**), PMe$_3$ (**5**), NH$_3$ (**6**) and N$_2$H$_4$ (**7**)) are discussed. Compounds **4** and **5** have a LS (singlet) state and compounds **6** and **7**, reportedly, a HS (quintet) ground state.[46–48] Furthermore, focus is placed on Fe^{III}(porphyrinato)Cl, FePCl (**8**) and, Fe^{III}(porphyrazinato)Cl, FePzCl (**9**), which have a sextet and a quartet ground state, respectively.

Structure relaxation and spin state energies of Fe(III) compounds 1–3

The optimization of the three Fe(III) molecules (**1**–**3**) led in all cases to the expected structural changes for the different spin states (Tables S-I–S-III of the Supplementary material to this paper). Comparison of the optimized structures of **1**–**3** indicated the existence of an expansion of the ligand sphere. Going from the doublet to the quartet state, first the equatorial ligands moved away from iron while the axial ligands stayed almost at the same position. In the sextet state, the equatorial ligands remained virtually at the same position, but the axial ligands (had to) moved out.

Comparing the vertical spin state energies, calculated on the experimental structure,[14] with results from the optimized ("relaxed") geometries, Table I, it is evident that the energy gap between different spin states decreased. In the case of compound **1**, the doublet state remained the spin ground state with the quartet state (from 22.5 kcal*·mol^{-1} "vertical" to 17.5 kcal·mol^{-1} "relaxed") and the sextet state (from 33.9 kcal·mol^{-1} "vertical" to 10.2 kcal·mol^{-1} "relaxed") in closer energetic proximity after geometry optimization. Molecule **2** has the quartet ground state, and here, the relative energies of the doublet and sextet states were reduced after structure relaxation. The same trends apply for the sextet ground state of complex **3**. For all complexes, after spin state relaxation, both OPBE and its recently developed successor S12g gave the correct spin ground state. Spin contamination was small for these complexes, and therefore, will not be discussed further.

The choice of exchange-correlation functional had an obvious influence on the geometry, with a tendency of S12g to give somewhat longer bond lengths than OPBE (Tables S-I–S-III). It should be noted that S12g gave structural parameters that were in excellent agreement with experimental values. Unlike the

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* 1 kcal = 4184 J

choice of functional, the influence of solvation on the geometrical parameters during the structural relaxation was not very significant, and it depended slightly on the system under consideration. In most cases, optimizations with COSMO gave slightly longer bonds, but without significant consequences for the spin-state splittings, Table I.

TABLE I. Spin state energies (kcal mol^{-1}) for Fe(III) molecules **1**–**3** using TZP basis set, with OPBE and S12g functionals, in vacuum and COSMO

Geo.[a]	SP[b]	Fe-(PyPepS)$_2$ **1**			Fe(tsalen)Cl **2**			Fe(N(CH$_2$-o-C$_6$H$_4$S)$_3$)(1MIm[b]) **3**		
		Doublet	Quartet	Sextet	Doublet	Quartet	Sextet	Doublet	Quartet	Sextet
OPBE	OPBE	0	17.1	10.2	6.5	0	3.9	6.6	7.9	0
	OPBE cosmo	0	19.4	13.0	9.3	0	6.9	7.9	7.4	0
	S12g	0	15.8	8.7	7.6	0	3.8	6.8	7.2	0
	S12g cosmo	0	18.2	11.6	10.2	0	6.4	8.2	6.8	0
OPBE cosmo	OPBE	0	18.8	13.1	5.2	0	2.9	6.2	7.5	0
	OPBE cosmo	0	17.4	10.2	9.7	0	7.7	8.0	7.2	0
	S12g	0	18.4	13.3	6.0	0	3.0	6.5	6.8	0
	S12g cosmo	0	17.1	10.6	10.2	0	7.4	8.3	6.5	0
S12g	OPBE	0	18.3	10.5	7.4	0	6.2	7.6	8.1	0
	OPBE cosmo	0	22.7	14.7	10	0	9.2	8.6	7.1	0
	S12g	0	15.4	8.7	7.5	0	6.6	6.5	7.0	0
	S12g cosmo	0	19.9	13.1	9.9	0	9.3	7.7	6.1	0
S12g cosmo	OPBE	0	17.5	10.6	7.0	0	4.7	7.5	8.4	0
	OPBE cosmo	0	20.5	14.9	11.2	0	6.7	8.8	7.2	0
	S12g	0	15.7	9.2	6.6	0	4.7	6.1	6.8	0
	S12g cosmo	0	18.8	13.7	10.4	0	6.5	7.6	5.9	0

[a]Geometry optimization with frozen core electrons; [b]subsequent single point calculations with all-electron basis sets

Structure relaxation and spin state energies of compounds 4–7

The spin state dependent structure relaxation for the Fe(II) compounds results in similar differences in Fe–ligand distances as for the Fe(III) compounds (Tables S-IV–S-VII). In the case of compounds **4**–**7**, the Fe–N, Fe–S and Fe–C distances were slightly elongated in comparison to the distances in the Fe(III) complexes due to the additional d-electron in the Fe(II) systems.

The spin ground states of the Fe(II) complexes **4** and **5** were correctly predicted using both the OPBE and S12g levels of theory (see Table II): the singlet state was the lowest in energy for both molecules, in agreement with expe-

TABLE II. Spin state energies (kcal mol^{-1}) for labile (*trans*) complexes **4** and **5** using TZP basis, with OPBE and S12g functionals, in vacuum and COSMO

Geo.[a]	SP[b]	*trans*-(Fe(NH)S$_4$)CO **4**			*trans*-(Fe(NH)S$_4$)PMe$_3$ **5**		
		Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
OPBE	OPBE	0	23.4	34.8	0	16.3	20.1
	OPBE cosmo	0	24.5	36.6	0	17.3	18.6
	S12g	0	19.1	28.0	0	14.5	17.7
	S12g cosmo	0	20.2	29.7	0	15.4	16.3
OPBE	OPBE	0	23.5	35.3	0	16.4	20.4
cosmo	OPBE cosmo	0	24.5	36.5	0	17.3	18.3
	S12g	0	19.4	29.1	0	15.1	19.1
	S12g cosmo	0	20.3	30.3	0	15.9	17.1
S12g	OPBE	0	23.4	34.2	0	19.6	19.4
	OPBE cosmo	0	24.3	36.4	0	20.3	19.2
	S12g	0	18.7	29.3	0	15.6	16.8
	S12g cosmo	0	19.6	31.4	0	16.3	16.6
S12g	OPBE	0	24.6	35.0	0	19.9	19.2
cosmo	OPBE cosmo	0	24.8	36.5	0	20.6	18.2
	S12g	0	20.4	30.8	0	15.8	17.1
	S12g cosmo	0	20.5	32.2	0	16.4	16.2

[a]Geometry optimization with frozen core electrons; [b]subsequent single point calculations with all-electron basis sets

rimental data. For compound **4**, the triplet and quintet states were significantly higher in energy. The energy differences between the different states were smaller for compound **5**. Similar to the Fe(III) complexes, spin contamination was small and will not be discussed any further. Similar to compounds **4** and **5**, after spin state structure relaxation, an LS ground state for iron complexes **6** and **7** was found, with IS and HS higher in energy. Unfortunately, the experimental determination of the spin states of compounds **6** and **7** were inconclusive, since anomalous high μ_{eff} values of 10–13 μ_B were measured that may indicate impurities, *e.g.*, by metallic iron, or oligomer formation. For compound **7** in solution, an HS state was observed,[48] but a compound similar to **7** showed a diamagnetic LS Fe center.[49] Moreover, indications of dimer formation of the ligand-free [(Fe(NH)S$_4$)] complex were observed.[47,48] Since different forms of the (Fe(NH)S$_4$)L complex in these studies were obtained, both forms for compounds **4**–**7**, *i.e.*, with the "*trans*" and "*meso*" form (see Fig. 2) had to be checked. For both forms of each of compounds **4**–**7**, an LS ground state was found, albeit with smaller spin-state splitting for compounds **6** and **7**. These findings could be traced back to the strength of the iron–ligand bond, which seems to be much weaker for compounds **6**/**7** than for compounds **4**/**5**. The weakly bound NH$_3$ and N$_2$H$_4$ ligands are easily exchanged with CH$_3$OH, solvent (THF) or CO.[48] These experimental data corroborate the present computed ligand-binding energies, which indicate strong and favorable binding of CO and P(Me)$_3$ to form the singlet ground state, but less favorable binding of the other ligands or spin states

(see Table S-VIII of the Supplementary material). Interestingly, the monomeric $Fe(NH)S_4$ complex without a ligand was predicted to have a triplet spin ground state in the *trans* form, with the other spin states or the *meso* form lying higher in energy by at least 7 kcal·mol^{-1}. The ligand-free complex may dimerize to give the experimentally observed HS state through ferromagnetic coupling. The latter process was not studied due to the complexity involved with ferromagnetic *versus* anti-ferromagnetic coupling of the many spin states that need to be considered. This was confirmed by a recent study using high-level *ab initio* methods that indeed found a singlet ground-state for these molecules.[50] In another recent study, "accurate" spin ground states for molecules **6** and **7** were found with the double hybrid B2PLYP functional, where an HS ground-state was obtained for molecule **6** with OPBE.[51] Since the last result is in disagreement with the results of the present study, molecules **6** and **7** were re-optimized using the OPBE functional with the geometries from their paper[51] as the starting point. The re-optimized structures resulted in spin state splittings that were in accordance with the previous study,[51] however, the structures were highly distorted representing only a local minimum on the potential energy surface (and *ca.* 5–20 kcal·mol^{-1} above the structures obtained here in Table III).
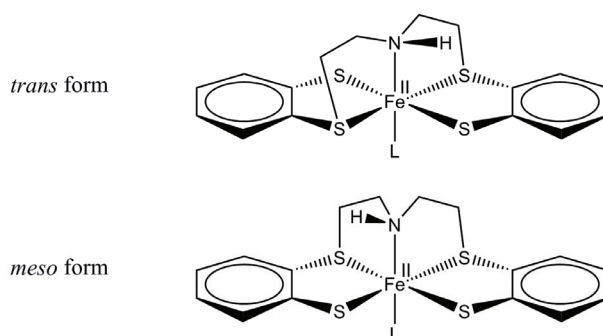

Fig. 2. Different forms of compounds **4**–**7**.

TABLE III. Spin state energies (kcal mol^{-1}) for labile (*meso*) complexes **6** and **7** using TZP basis, with OPBE and S12g functionals, in vacuum and COSMO

Geo.[a]	SP[b]	*meso*-$(Fe(NH)S_4)NH_3$ (**6**)			*meso*-$(Fe(NH)S_4)N_2H_4$ (**7**)		
		Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
OPBE	OPBE	0	10.3	6.6	0	11.3	6.6
	OPBE cosmo	0	10.1	3.9	0	10.7	4.4
	S12g	0	7.7	2.6	0	8.5	2.5
	S12g cosmo	0	7.4	–0.1	0	7.9	0.3
OPBE	OPBE	0	10.6	7.2	0	11.5	7.1
cosmo	OPBE cosmo	0	9.9	3.5	0	10.1	3.8
	S12g	0	7.9	3.5	0	9.7	3.6
	S12g cosmo	0	7.0	–0.2	0	8.2	0.5

TABLE III. Continued

Geo.[a]	SP[b]	meso-(Fe(NH)S$_4$)NH$_3$ (6)			meso-(Fe(NH)S$_4$)N$_2$H$_4$ (7)		
		Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
S12g	OPBE	0	10.1	7.5	0	11.1	7.6
	OPBE cosmo	0	10.7	5.7	0	11.0	6.8
	S12g	0	8.4	5.3	0	9.3	5.3
	S12g cosmo	0	8.7	3.4	0	9.2	4.6
S12g	OPBE	0	10.1	6.8	0	10.8	6.6
cosmo	OPBE cosmo	0	10.5	4.4	0	10.4	5.2
	S12g	0	8.7	4.9	0	9.4	4.6
	S12g cosmo	0	8.8	2.4	0	8.9	3.2

[a]Geometry optimization with frozen core electrons; [b]subsequent single point calculations with all-electron basis sets

As in the case of the previous investigated molecules **1**–**3**, after optimization with S12g, somewhat longer bond lengths were obtained in comparison with the OPBE geometries. Nevertheless, both of them are again in good agreement with the experimental data (Tables S-IV–S-VII). In contrast to the Fe(II) complexes **1**–**3**, the Fe(III) P450 model systems **4**–**7** are prone to the influence of solvent (COSMO calculations) on the spin state ordering, Tables II and III. Calculations with the COSMO solvation model revealed a tendency to favor the HS state for complexes **5**–**7**, and the LS state for complex **4**.

Iron porphyrin chloride and the porphyrazine analogue

The structures of FePCl (**8**) and FePzCl (**9**) were separately optimized in C$_{4v}$ symmetry for each spin state. Similarly to previous results,[30,52,53] it was found that the porphyrin core size increased when going from the LS to the HS state, while the Fe–Cl distance increased from the LS to the IS state, and then was slightly decreased in the HS state (Tables S-IX and S-X of the Supplementary material).

OPBE and S12g predicted the correct sextet spin ground state for both, FePCl and FePzCl (see Table IV). In the case of FePCl, a sextet ground state was predicted with the quartet higher in energy and *vice versa* for FePzCl, the quartet state was lower in energy. In both cases, the LS state was considerably higher in energy.

COSMO calculations revealed a clear and unambiguous solvent effect on the electronic structure, Table IV. Introduction of the solvent favored the LS state, and as such had small effects on the spin ground state of molecule **9** that has a quartet ground state and a sextet quartet state that is similar in energy. In contrast, for molecule **8**, that is in an HS state experimentally and has a low-lying quartet state, the quartet state is stabilized to the extent that it becomes the ground state within all COSMO calculations. Of course, it should be added that the spin-state splittings were investigated here through looking at the electronic energy and

hence, enthalpy and entropy effects were ignored. Both of these favor the high-
-spin states. Finally, S12g once again showed excellent agreement with the spin
state energetics obtained at the OPBE level of theory.

TABLE IV. Spin state energy differences (kcal mol^{-1}, TZP basis) for FePCl (**8**) and FePzCl
(**9**), with OPBE and S12g functionals, in vacuum and COSMO

Geo.[a]	SP[b]	FePCl			FePzCl		
		Doublet	Quartet	Sextet	Doublet	Quartet	Sextet
OPBE	OPBE	18.4	3.9	0	12.5	0	3.7
	OPBE cosmo	16.3	−1.0	0	15.6	0	7.6
	S12g	15.7	1.5	0	12.8	0	4.9
	S12g cosmo	13.8	−2.9	0	15.8	0	8.6
OPBE	OPBE	18.0	4.8	0	11.6	0	2.9
cosmo	OPBE cosmo	16.9	−1.7	0	16.6	0	8.2
	S12g	15.0	2.3	0	11.8	0	4.2
	S12g cosmo	14.1	−3.6	0	16.5	0	9.2
S12g	OPBE	18.6	4.0	0	12.7	0	3.7
	OPBE cosmo	16.3	−0.7	0	15.7	0	7.5
	S12g	15.4	1.5	0	12.6	0	5.0
	S12g cosmo	13.4	−2.8	0	15.4	0	8.6
S12g	OPBE	18.3	4.5	0	12.0	0	3.2
cosmo	OPBE cosmo	17.1	−1.6	0	16.8	0	8.1
	S12g	15.0	2.0	0	11.8	0	4.6
	S12g cosmo	14.0	−3.5	0	16.3	0	9.2

[a]Geometry optimization with frozen core electrons; [b]subsequent single point calculations with all-electron basis sets

CONCLUSIONS

Within this paper, an extension of previous validation[14] of DFAs for a
correct description of the spin states of Fe(II) and Fe(III) complexes is presented.
In the present contribution, structure relaxation of the LS, IS and HS states of the
iron compounds was allowed separately at the OPBE and S12g levels of theory
and thereby, a more stringent test on the reliability of functionals for providing
spin ground states of iron complexes was performed.

A detailed comparison with the already proven OPBE DFA for spin state
energetics, and experimental findings, revealed that S12g performed remarkably
well and thus, represents a very promising tool for studying spin states in com-
plicated transition metal systems. Moreover, for all iron complexes under inves-
tigation, S12g gave a good match with experimental geometries and thus, could
be considered as a good starting point for the investigation of transition metal
compounds.

SUPPLEMENTARY MATERIAL

Selected bond lengths, OPBE/TZP ligand binding energies, as well as coordinates of
optimized structures (as additional supplementary file), are available electronically from
http://www.shd.org.rs/JSCS/ or from the corresponding author on request.

ИЗВОД

РЕЛАКСАЦИЈА СПИНСКИХ СТАЊА КОД КОМПЛЕКСА ГВОЖЂА: СЛУЧАЈ ЗА OPBE И S12g ФУНКЦИОНАЛЕ

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Структуре девет комплекса гвожђа који показују разноврсност експериментално одређених основних спинских стања оптимизоване су теоријом функционала густине (DFT), а затим анализиране коришћењем различитих функционала. Извршена је обимна валидациона студија новог S12g функционала, са дискусијом о утицају окружења, гео-метрије, као и његових перформанси у односу на OPBE функционал који се већ показао као добар. OPBE и S12g тачно предвиђају основно спинско стање код свих испитиваних комплекса гвожђа. Како се S12g показао изузетно добро, он се може сматрати поузда-ним за проучавање енергетике спинских стања у компликованим системима прелазних метала.

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