

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 are optimized and analysed with Density Functional Theory (DFT). An extensive validation study of the new S12g functional is performed, with the discussion concerning the influence of the environment, geometry and its overall performance based on the comparison with the well proven OPBE functional. The OPBE and S12g functionals give the correct spin ground state for all investigated iron complexes. Since S12g performs remarkably well it can be considered a reliable tool for studying spin state energetics in complicated transition metal systems.

Keywords: Density Functional Theory; Fe(II) and Fe(III) coordination compounds; validation study; spin states.

RUNNING TITLE: SPIN STATE ENERGETICS OF IRON COMPLEXES

INTRODUCTION

Spin is an intrinsic and inherent property of atoms and molecules.¹ Most of the 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 have usually either 5 or 6 d-electrons that can be distributed in 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 the intermediate (IS) spin state. Since HS, IS and LS complexes usually display quite different structural, spectral

35 and magnetic properties, and often also reactivity, it is of the utmost importance to have both
36 experimental and theoretical methods to correctly determine the spin ground state of the
37 system. However, both experiment and theory have difficulties and problems, and many
38 studies have been devoted to this issue in the last decade.^{2, 3, 4, 5}

39 From a broad palette of quantum mechanical methods, Density Functional Theory (DFT)⁶
40 ^{7, 8} emerged into the mainstream, mainly because it gives a good compromise between the
41 accuracy of the results and the computational efficiency.^{9, 10, 11} However, although DFT gives
42 in principle exact energy, the universal functional is still unknown, leading to density
43 functional approximations (DFAs). These DFAs are parameterized for different properties and,
44 noteworthy, spin-state energies were not included in the development for most of nowadays
45 available DFAs.¹² It has been shown that the accuracy of the results strongly depends of the
46 choice of the DFAs, but also on the basis set that is used.^{1, 3, 13, 14} Early pure functionals like
47 LDA^{15, 16, 17}, BP86,^{18, 19} BLYP,^{19, 20} or PW91^{21, 22} have a tendency to favor LS states,¹⁴ while
48 hybrid functionals like B3LYP^{23, 24}, PBE0²⁵ and M06^{26, 27} systematically favor HS.¹⁴ For the
49 reliable prediction of the correct spin ground state from a number of close lying states,
50 OPBE¹⁴ emerged to be one of the best functionals for the job.²⁸ Recently Swart constructed a
51 new density functional that combines the best of OPBE (spin states, reaction barriers) with the
52 best of PBE (weak interactions) into the S12g⁵ DFA.

53

54 Previously we reported the relative spin state energies of seven iron complexes (**1-7**,
55 Figure 1) on OLYP^{20, 29} optimized geometries (**1-3**) and on crystal structures (**4-7**) with a
56 variety of DFAs and already showed the good performance of OPBE for vertical spin state
57 splittings.¹⁴

58

59

<Figure 1>

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61 Herein, we present a detailed DFT study on OPBE optimized geometries of iron
62 complexes (**1-7**) with experimentally established spin ground states, ranging from singlet to
63 sextet, and extended it with two iron porphyrinato complexes (**8, 9**, Figure 1) that have been
64 reported to have different electronic ground state in spite of their similarity.^{30, 31, 32}

65 Furthermore, a comprehensive validation study of the S12g DFA,⁵ together with the
66 examination of the influence of the chemical environment is performed on all investigated
67 complexes.

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METHODOLOGY

70 All DFT calculations were performed with the Amsterdam Density Functional (ADF) suite
71 of program.^{33,34} MOs were expanded in an uncontracted set of Slater type orbitals (STOs) of
72 triple- ζ quality containing diffuse functions (TZP)³⁵ and one set of polarization functions.
73 Core electrons (1s for 2nd period, 1s2s2p for 3rd-4th period) were not treated explicitly during
74 the geometry optimizations (frozen core approximation), as it was shown to have a negligible
75 effect on the obtained geometries.³⁶ An auxiliary set of s, p, d, f, and g STOs was used to fit
76 the molecular density and to represent the Coulomb and exchange potentials accurately for
77 each SCF cycle.

78 Energies and gradients were calculated using the OPBE and S12g functionals, in the gas
79 phase and with the COSMO^{37, 38, 39} dielectric continuum model for the solvent environment.
80 Geometries were optimized with the QUILD program⁴⁰ using adapted delocalized
81 coordinates⁴¹ until the maximum gradient component was less than 10^{-4} a.u. Subsequent
82 single point calculations that utilize all electron basis set have been performed on all
83 optimized geometries, with OPBE and S12g.

84

85

RESULTS AND DISCUSSION

86

87 The total set of molecules consists both of Fe(III) (**1–3**, **8–9**) and Fe(II) (**4–7**) complexes,
88 and show a diversity of experimentally observed spin ground states. A thorough examination
89 with the OPBE and S12g functionals, in the gas phase and the COSMO solvent environment,
90 is performed. We will start our discussion focusing on the influence of the structure
91 relaxation on the spin states of Fe(III)-complexes **1–3**.⁴² Experimentally, Fe-(PyPepS)₂ (**1**,
92 PyPepSH₂=N-2-mercaptophenyl-2'-pyridine-carboxamide) has a LS doublet ground state,⁴³
93 Fe(tsalen)Cl (**2**, tsalen = N,N'-ethylenebis-(thio-salicylideneiminato)) an intermediate spin
94 (IS), quartet ground state⁴⁴ and Fe(N(CH₂-o-C₆H₄S)₃)(1-Me-imidazole) (**3**) a HS sextet
95 ground state.⁴⁵ Then we will discuss the Fe(II)-complexes ((Fe(NH)S₄)L, (NH)S₄=bis(2-((2-
96 mercaptophenyl)thio)ethyl)amine, L=CO (**4**), PMe₃ (**5**), NH₃ (**6**) and N₂H₄ (**7**)). Compounds
97 **4–5** have a LS (singlet) state and compounds **6–7** reportedly a HS (quintet) ground state.^{46, 47,}
98 ⁴⁸ Furthermore, we will focus on Fe^{III}(porphyrinato)Cl, FePcCl (**8**) and,
99 Fe^{III}(porphyrinato)Cl, FePzCl (**9**), which have a sextet and a quartet ground state,
100 respectively.

101

102 *Structure relaxation and spin state energies of Fe(III) compounds 1-3*

103

104 The optimization of the three Fe(III) molecules (**1-3**) leads in all cases to the expected
105 structural changes for the different spin states (Tables S1-S3). Comparison of the optimized
106 structures of **1-3** indicates the existence of an expansion of the ligand sphere. Going from the
107 doublet to the quartet state, first the equatorial ligands move away from iron while the axial
108 ligands stay almost at the same position. In the sextet state, the equatorial ligands remain
109 virtually at the same position, but the axial ligands (have to) move out.

110

111 Comparing the vertical spin state energies, calculated on the experimental structure,¹⁴ with
112 results from the optimized (“relaxed”) geometries, Table 1, it is evident that the energy gap
113 between different spin states decreases. In the case of compound **1**, the doublet state remains
114 the spin ground state with the quartet state (from 22.5 kcal·mol⁻¹ “vertical” to 17.5 kcal·mol⁻¹
115 “relaxed”) and the sextet state (from 33.9 kcal·mol⁻¹ “vertical” to 10.2 kcal·mol⁻¹ “relaxed”) in
116 closer energetic proximity after geometry optimization. Molecule **2** has the quartet ground
117 state, and also here are the relative energies of the doublet and sextet states reduced after
118 structure relaxation. The same trends apply for the sextet ground state of complex **3**. For all
119 complexes, after the spin state relaxation, both OPBE and its recently developed successor,
120 S12g, give the correct spin ground state. Spin contamination is small for these complexes,
121 and therefore shall not be discussed any further.

122

123 The choice of exchange-correlation functional has an obvious influence on the geometry,
124 with a tendency of S12g to give somewhat longer bond lengths than OPBE (Tables S1-S3). It
125 should be noted that S12g gives structural parameters that are in excellent agreement with
126 experimental values. Unlike the choice of functional, the influence of solvation on the
127 geometrical parameters during the structural relaxation was not very significant, and it
128 depends slightly on system under consideration. In most cases, optimizations with COSMO
129 gave slightly longer bonds, but without significant consequences for the spin-state splittings,
130 Table I.

131

132 <Table I>

133

134 *Structure relaxation and spin state energies of compounds 4-7*

135

136 The spin state dependent structure relaxation for the Fe(II) compounds results in similar
137 differences in Fe-ligand distances as for the Fe(III) compounds (Tables S4-S7). In the case of
138 compounds **4-7**, the Fe-N, Fe-S and Fe-C distances are slightly elongated in comparison to
139 the distances in Fe(III) complexes due to the additional *d*-electron in Fe(II) systems.

140
141 The spin ground state of the Fe(II) complexes **4** and **5** is correctly predicted using both
142 OPBE and S12g levels of theory (see Table II): the singlet state is the lowest in energy for
143 both molecules, in agreement with experimental data. For compound **4**, the triplet and quintet
144 states are significantly higher in energy. The energy differences between the different states
145 are smaller for compound **5**. Similar to the Fe(III) complexes, spin contamination is small and
146 shall not be discussed any further. Similar to compounds **4** and **5**, we found after spin state
147 structure relaxation a LS ground state for iron complexes **6** and **7**, with the IS and HS higher
148 in energy. Unfortunately, the experimental determination of the spin states of compounds **6**
149 and **7** is inconclusive, since anomalous high μ_{eff} values of 10-13 μ_{B} have been measured that
150 may indicate impurities, e.g. by metallic iron, or oligomer formation. For compound **7** in
151 solution, a HS state was observed,⁴⁸ but a compound similar to **7** showed a diamagnetic LS
152 Fe center.⁴⁹ Moreover, indications of dimer formation of the ligand-free [(Fe(NH)S₄)]-
153 complex were observed.^{47, 48} Since the different forms of the (Fe(NH)S₄)L complex in these
154 studies were obtained, we have checked both forms for compounds **4-7**, i.e. with the “trans”
155 and “meso” form (see Figure 2). For both forms of each of compounds **4-7** we found a LS
156 ground state, albeit with smaller spin-state splitting for compounds **6** and **7**. These findings
157 can be traced back to the strength of the iron-ligand bond, which seems to be much weaker
158 for compounds **6/7** than for compounds **4/5**. The weakly bound NH₃ and N₂H₄ ligands are
159 easily exchanged with CH₃OH, solvent (THF) or CO.⁴⁸ These experimental data corroborate
160 our computed ligand-binding energies, which indicate strong and favorable binding of CO
161 and P(Me)₃ to form the singlet ground state, but less favorable binding of the other ligands or
162 spin states (see Table S10). Interestingly, the monomeric Fe(NH)S₄ complex without a ligand
163 is predicted to have a triplet spin ground state in the trans form, with the other spin states or
164 the meso form lying higher in energy by at least 7 kcal·mol⁻¹. The ligand-free complex may
165 dimerize to give the experimentally observed HS state through ferromagnetic coupling. The
166 latter process has not been studied due to the complexity involved with ferromagnetic versus
167 anti-ferromagnetic coupling of the many spin states that need to be considered. This is
168 confirmed by a recent study using high-level *ab initio* methods that indeed found a singlet

169 ground-state for these molecules.⁵⁰ In another recent study, “accurate” spin ground states for
170 molecules **6** and **7** were found with the double hybrid B2PLYP functional, where a HS
171 ground-state was obtained for molecule **6** with OPBE.⁵¹ Since the last result is in
172 disagreement with our study, we re-optimized molecules **6** and **7** using the OPBE functional
173 with the geometries from their paper⁵¹ as starting point. The reoptimized structures resulted in
174 spin state splittings that were in accordance with the previous study,⁵¹ however, the structures
175 were highly distorted representing only a local minimum on the potential energy surface (and
176 ca. 5-20 kcal·mol⁻¹ above the structures obtained here for Table III).

177

178 <Figure 2>

179

180 As in the case of previous investigated molecules **1-3**, after optimization with S12g,
181 somewhat longer bond lengths have been obtained in comparison with OPBE geometries.
182 Nevertheless both of them are again in good agreement with the experimental data (Tables
183 S4-S7). In contrast to the Fe(II) complexes (**1-3**), the Fe(III) P450 model systems (**4-7**) are
184 prone to the influence of solvent (COSMO calculations) on spin state ordering, Table II and
185 Table III. Calculations with COSMO solvation model revealed a tendency to favor the HS
186 state for complexes **5-7**, and the LS state for complex **4**.

187

188 <Table II>

189 <Table III>

190

191 *Iron porphyrin chloride and the porphyrazine analogue*

192

193 The structures of FePcCl (**8**) and FePzCl (**9**) were optimized in C_{4v} symmetry, separately
194 for each spin state. Similarly to previous results,^{52, 53,54} it was found that the porphyrin core
195 size increases when going from the LS to the HS state, while the Fe-Cl distance increases
196 from the LS to IS state, and then slightly decreases in the HS state (Tables S8-S9).

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

201

202 COSMO calculations revealed a clear and unambiguous solvent effect on the electronic

203 structure, Table IV. Introduction of the solvent favors the LS state, and as such have small
204 effects on the spin ground state of molecule **9** that has a quartet ground state and a sextet
205 quartet state that is close in energy. In contrast, for molecule **8**, that is in a HS experimentally
206 and has low lying quartet state, the quartet state is stabilized to the extent that it becomes the
207 ground state within all COSMO calculations. Of course, it should be added that we have been
208 investigating the spin-state splittings through looking at the electronic energy, and hence
209 ignoring the enthalpy and entropy effects. Both of these favor the high-spin states. Finally,
210 S12g once again shows excellent agreement with spin state energetics obtained with OPBE
211 level of theory.

212
213 <Table IV>

214 215 CONCLUSION

216 Within this paper the extension of our previous validation¹⁴ of DFAs for a correct
217 description of spin states of Fe(II) and Fe(III) complexes is presented. In the present
218 contribution we allow the structure relaxation of the LS, IS and HS states of the iron
219 compounds separately at OPBE and S12g levels of theory, thereby performing a more
220 stringent test on the reliability of functionals for providing spin ground states of iron
221 complexes.

222 A detailed comparison with the already proven OPBE DFA for spin state energetics, and
223 experimental findings, revealed that S12g performs remarkably well, and thus represents a
224 very promising tool for studying spin states in complicated transition metal systems.
225 Moreover, for all iron complexes under investigation S12g gives a good match with
226 experimental geometries, and thus can be considered as good starting point to investigate
227 transition metal compounds.

228
229 *Acknowledgments.* The following organizations are thanked for financial support: the
230 Ministerio de Ciencia e Innovación (MICINN, project CTQ2011-25086/BQU), the Ministerio
231 de Economía y Competitividad (MINECO, project CTQ2014-59212/BQU) and the DIUE of
232 the Generalitat de Catalunya (project 2014SGR1202, and Xarxa de Referència en Química
233 Teòrica i Computacional). Financial support was provided by MICINN and the FEDER fund
234 (European Fund for Regional Development) under grant UNGI10-4E-801, and the Serbian
235 Ministry of Education and Science (Grant No. 172035). This work was performed in the

236 framework of the COST action CM1305 “Explicit Control Over Spin-states in Technology
237 and Biochemistry (ECOSTBio)” (STSM reference: ECOST-STSM-CM1305-27360). We
238 would like to thank Dr. A.W. Ehlers and Prof. K. Lammertsma (VU Amsterdam,
239 Netherlands) for help and fruitful discussions in the initial stages of this study.

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ИЗВОД

**РЕЛАКСАЦИЈА СПИНСКИХ СТАЊА КОД КОМПЛЕКСА ГВОЖЂА: СЛУЧАЈ
ЗА ОРВЕ 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 анализирани коришћењем различитих функционала. Извршена је обимна валидациона студија новог S12g функционала, са дискусијом о утицају окружења, геометрије, као и његових перформанси у односу на ОРВЕ функционал који се већ показао као добар. ОРВЕ и S12g тачно предвиђају основно спинско стање код свих испитиваних комплекса гвожђа. Како се S12g показао изузетно добро, он се може сматрати поузданим за проучавање енергетике спинских стања у компликованим системима прелазних метала.

268 Table captions:

- 269 • Table I Spin state energies (kcal mol⁻¹) for Fe(III) molecules **1-3** using TZP basis set,
270 with OPBE and S12g functionals, in vacuum and COSMO.
- 271 • Table II Spin state energies (kcal mol⁻¹) for labile (“trans”) complexes **4** and **5** using
272 TZP basis, with OPBE and S12g functionals, in vacuum and COSMO.
- 273 • Table III Spin state energies (kcal mol⁻¹) for labile (“meso”) complexes **6** and **7** using
274 TZP basis, with OPBE and S12g functionals, in vacuum and COSMO.
- 275 • Table IV Spin state energy differences (kcal mol⁻¹, TZP basis) for FePCl (**8**) and
276 FePzCl (**9**), with OPBE and S12g functionals, in vacuum and COSMO.

277 Table I. Spin state energies (kcal mol⁻¹) for Fe(III) molecules **1-3** using TZP basis set, with
 278 OPBE and S12g functionals, in vacuum and COSMO.

279

Geo.*	SP [†]	Fe-(PyPepS) ₂ 1			Fe(tsalen)Cl 2			Fe(N(CH ₂ -o-C ₆ H ₄ S) ₃)(1MIm ^b) 3		
		<i>doublet</i>	<i>quartet</i>	<i>sextet</i>	<i>doublet</i>	<i>quartet</i>	<i>sextet</i>	<i>doublet</i>	<i>quartet</i>	<i>sextet</i>
OPBE	OPBE	0	17.1	10.2	6.5	0	3.9	6.6	7.9	0
	OPBE	0	19.4	13.0	9.3	0	6.9	7.9	7.4	0
	cosmo									
	S12g	0	15.8	8.7	7.6	0	3.8	6.8	7.2	0
	S12g	0	18.2	11.6	10.2	0	6.4	8.2	6.8	0
	cosmo									
OPBE	OPBE	0	18.8	13.1	5.2	0	2.9	6.2	7.5	0
	OPBE	0	17.4	10.2	9.7	0	7.7	8.0	7.2	0
	cosmo									
	S12g	0	18.4	13.3	6.0	0	3.0	6.5	6.8	0
	S12g	0	17.1	10.6	10.2	0	7.4	8.3	6.5	0
	cosmo									
S12g	OPBE	0	18.3	10.5	7.4	0	6.2	7.6	8.1	0
	OPBE	0	22.7	14.7	10	0	9.2	8.6	7.1	0
	cosmo									
	S12g	0	15.4	8.7	7.5	0	6.6	6.5	7.0	0
	S12g	0	19.9	13.1	9.9	0	9.3	7.7	6.1	0
	cosmo									
S12g	OPBE	0	17.5	10.6	7.0	0	4.7	7.5	8.4	0
	OPBE	0	20.5	14.9	11.2	0	6.7	8.8	7.2	0
	cosmo									
	S12g	0	15.7	9.2	6.6	0	4.7	6.1	6.8	0
	S12g	0	18.8	13.7	10.4	0	6.5	7.6	5.9	0
	cosmo									

280

* Geometry optimization with frozen core electrons

† Subsequent single point calculations with full electron basis sets

281 Table II. Spin state energies (kcal mol⁻¹) for labile (“trans”) complexes **4** and **5** using TZP
 282 basis, with OPBE and S12g functionals, in vacuum and COSMO.

283

Geo.‡	SP§	<i>trans</i> -(Fe(NH)S ₄)CO 4			<i>trans</i> -(Fe(NH)S ₄)PMe ₃ 5		
		<i>singlet</i>	<i>triplet</i>	<i>quintet</i>	<i>singlet</i>	<i>triplet</i>	<i>quintet</i>
OPBE	OPBE	0	23.4	34.8	0	16.3	20.1
	OPBE	0	24.5	36.6	0	17.3	18.6
	cosmo						
	S12g	0	19.1	28.0	0	14.5	17.7
	S12g	0	20.2	29.7	0	15.4	16.3
	cosmo						
OPBE	OPBE	0	23.5	35.3	0	16.4	20.4
	OPBE	0	24.5	36.5	0	17.3	18.3
	cosmo						
	S12g	0	19.4	29.1	0	15.1	19.1
	S12g	0	20.3	30.3	0	15.9	17.1
	cosmo						
S12g	OPBE	0	23.4	34.2	0	19.6	19.4
	OPBE	0	24.3	36.4	0	20.3	19.2
	cosmo						
	S12g	0	18.7	29.3	0	15.6	16.8
	S12g	0	19.6	31.4	0	16.3	16.6
	cosmo						
S12g	OPBE	0	24.6	35.0	0	19.9	19.2
	OPBE	0	24.8	36.5	0	20.6	18.2
	cosmo						
	S12g	0	20.4	30.8	0	15.8	17.1
	S12g	0	20.5	32.2	0	16.4	16.2
	cosmo						

‡ Geometry optimization with frozen core electrons

§ Subsequent single point calculations with full electron basis sets

284 Table III. Spin state energies (kcal mol⁻¹) for labile (“meso”) complexes **6** and **7** using TZP
 285 basis, with OPBE and S12g functionals, in vacuum and COSMO.

286

Geo. ^{**}	SP ^{††}	<i>meso</i> -(Fe(NH)S ₄)NH ₃ 6			<i>meso</i> -(Fe(NH)S ₄)N ₂ H ₄ 7		
		<i>singlet</i>	<i>triplet</i>	<i>quintet</i>	<i>singlet</i>	<i>triplet</i>	<i>quintet</i>
OPBE	OPBE	0	10.3	6.6	0	11.3	6.6
	OPBE	0	10.1	3.9	0	10.7	4.4
	cosmo						
	S12g	0	7.7	2.6	0	8.5	2.5
	S12g	0	7.4	-0.1	0	7.9	0.3
OPBE	OPBE	0	10.6	7.2	0	11.5	7.1
	OPBE	0	9.9	3.5	0	10.1	3.8
	cosmo						
	S12g	0	7.9	3.5	0	9.7	3.6
	S12g	0	7.0	-0.2	0	8.2	0.5
S12g	OPBE	0	10.1	7.5	0	11.1	7.6
	OPBE	0	10.7	5.7	0	11.0	6.8
	cosmo						
	S12g	0	8.4	5.3	0	9.3	5.3
	S12g	0	8.7	3.4	0	9.2	4.6
S12g	OPBE	0	10.1	6.8	0	10.8	6.6
	OPBE	0	10.5	4.4	0	10.4	5.2
	cosmo						
	S12g	0	8.7	4.9	0	9.4	4.6
	S12g	0	8.8	2.4	0	8.9	3.2

287

^{**} Geometry optimization with frozen core electrons

^{††} Subsequent single point calculations with full electron basis sets

288 Table IV. Spin state energy differences (kcal mol⁻¹, TZP basis) for FePzCl (**8**) and FePzCl (**9**),
 289 with OPBE and S12g functionals, in vacuum and COSMO.

Geo. ^{‡‡}	SP ^{§§}	<i>FePzCl</i>			<i>FePzCl</i>		
		<i>doublet</i>	<i>quartet</i>	<i>sextet</i>	<i>doublet</i>	<i>quartet</i>	<i>sextet</i>
OPBE	OPBE	18.4	3.9	0	12.5	0	3.7
	OPBE	16.3	-1.0	0	15.6	0	7.6
	cosmo						
	S12g	15.7	1.5	0	12.8	0	4.9
S12g	S12g	13.8	-2.9	0	15.8	0	8.6
	cosmo						
	OPBE	18.0	4.8	0	11.6	0	2.9
	OPBE	16.9	-1.7	0	16.6	0	8.2
cosmo	cosmo	15.0	2.3	0	11.8	0	4.2
	S12g	14.1	-3.6	0	16.5	0	9.2
	S12g	18.6	4.0	0	12.7	0	3.7
	OPBE	16.3	-0.7	0	15.7	0	7.5
S12g	cosmo	15.4	1.5	0	12.6	0	5.0
	S12g	13.4	-2.8	0	15.4	0	8.6
	cosmo	18.3	4.5	0	12.0	0	3.2
	OPBE	17.1	-1.6	0	16.8	0	8.1
S12g	cosmo	15.0	2.0	0	11.8	0	4.6
	S12g	14.0	-3.5	0	16.3	0	9.2
	cosmo						
	S12g						

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^{‡‡} Geometry optimization with frozen core electrons

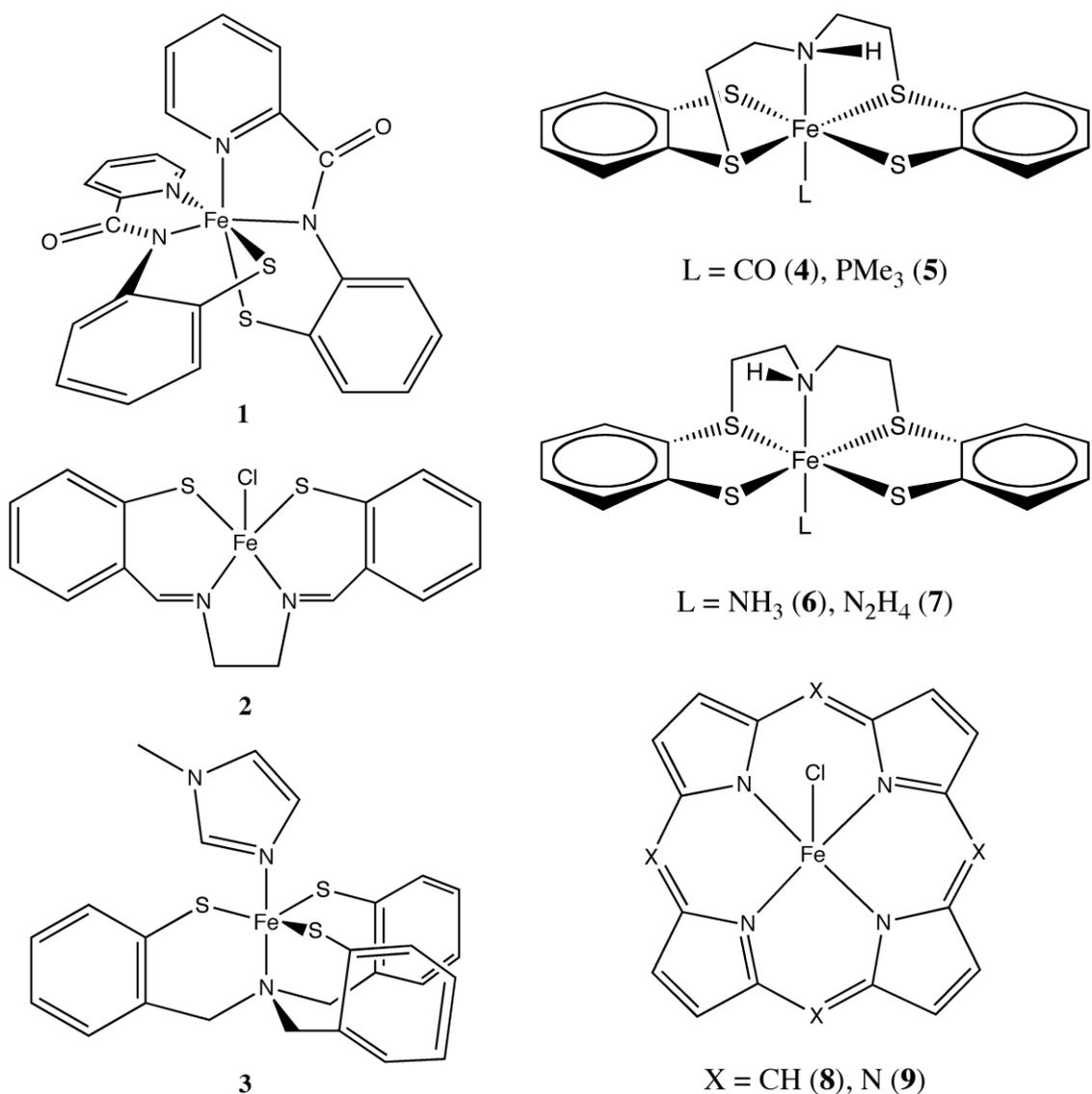
^{§§} Subsequent single point calculations with full electron basis sets

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292 Figure captions:

- 293 • Figure 1. Fe-(PyPepS)₂ **1** (PyPepSH₂ = N-2-mercaptophenyl-2'-pyridine-
294 carboxamide); Fe(tsalen)Cl **2** (tsalen =N,N'-ethylenebis-(thio-salicylideneiminato));
295 Fe(N(CH₂-o-C₆H₄S)₃)(1-Me-imidazole) **3**; (Fe(NH)S₄)L **4** (L=CO), **5** (PMe₃), **6**
296 (NH₃), **7** (N₂H₄) ((NH)S₄ = bis(2-((2-mercaptophenyl)thio)ethyl)amine); Iron
297 porphyrin chloride (**8**, FePCL) and iron porphyrazine chloride (**9**, FePzCl).
- 298 • Figure 2. Different forms of compounds **4-7**.

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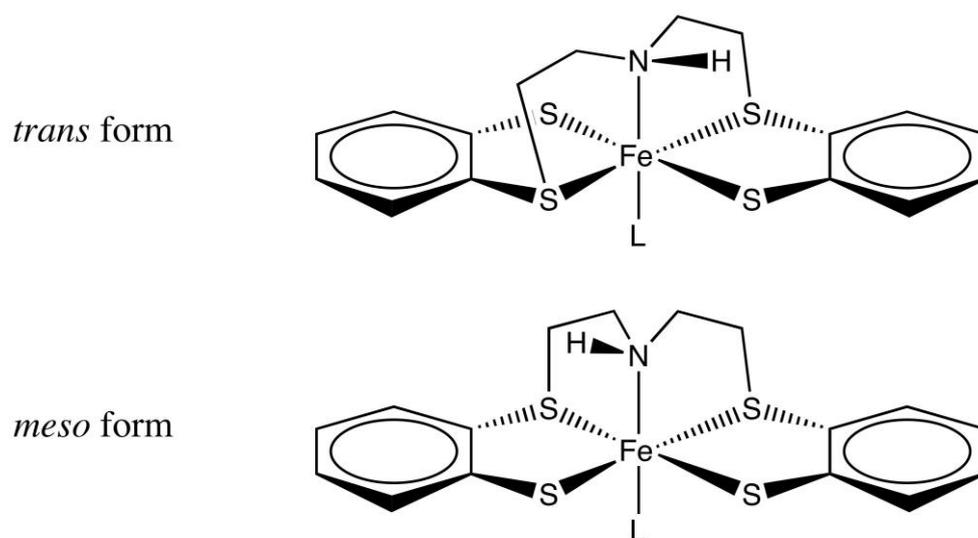


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302 **Figure 1.** Fe-(PyPepS)₂ **1** (PyPepSH₂ = N-2-mercaptophenyl-2'-pyridine-carboxamide);
 303 Fe(tsalen)Cl **2** (tsalen =N,N'-ethylenebis-(thio-salicylideneiminato)); Fe(N(CH₂-o-
 304 C₆H₄S)₃)(1-Me-imidazole) **3**; (Fe(NH)S₄)L **4** (L=CO), **5** (PMe₃), **6** (NH₃), **7** (N₂H₄) ((NH)S₄
 305 = bis(2-((2-mercaptophenyl)thio)ethyl)amine); Iron porphyrin chloride (**8**, FePcCl) and iron
 306 porphyrazine chloride (**9**, FePzCl).

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Figure 2. Different forms of compounds **4-7**.

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