

Full Articles

Computational modeling of spin crossover phenomenon in adducts of iron *bis*-chelates with *o*-diiminobenzoquinones

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A density functional B3LYP*/6-311++G(d,p) quantum chemical study of the interaction of Fe^{II} complexes with *o*-diiminobenzoquinones showed that adduct formation is accompanied by oxidation of the metal ion and conversion of the redox-active ligand to the semiquinonate form. Variation of substituents at nitrogen atoms of the *bis*-chelate and diimine made it possible to reveal the spin-crossover complexes. The nature and strength of the exchange interactions between the unpaired electrons of paramagnetic centers of the adducts studied depend on the spin state of their isomers and on the type of the iron complex.

Key words: quantum chemical calculations, spin crossover, iron *bis*-chelates, redox-active ligands, magnetic properties, density functional theory.

Transition-metal coordination compounds whose magnetic properties can be switched by external stimuli represent a unique platform for the design of nonvolatile, high-capacity molecular memory devices,^{1–4} color displays,⁵ and contrast agents for magnetic resonance imaging.⁶ This type of compounds is expected to find application in quantum information technologies.^{7–9} Most often, the spin states of metal complexes are switched by the spin crossover (SCO) mechanism, *i.e.*, the spin state of a metal ion changes upon variation of temperature or pressure, or by irradiation.^{3,10,11} The effect was discovered¹² in 1931 and has been studied for a variety of transition metal complexes.

The necessary conditions for SCO include (i) close values of the electron pairing energies and the splitting parameters of the low-spin (LS) and high-spin (HS) states and (ii) rather narrow energy gap between these states. Although the properties of the SCO materials are governed by cooperative effects (molecular packing in crystals, type of counterions, presence of solvated solvent molecules), the phenomenon is caused by rearrangements of the electronic configurations of single molecules. This allows quantum chemistry methods to be used in the search for SCO.

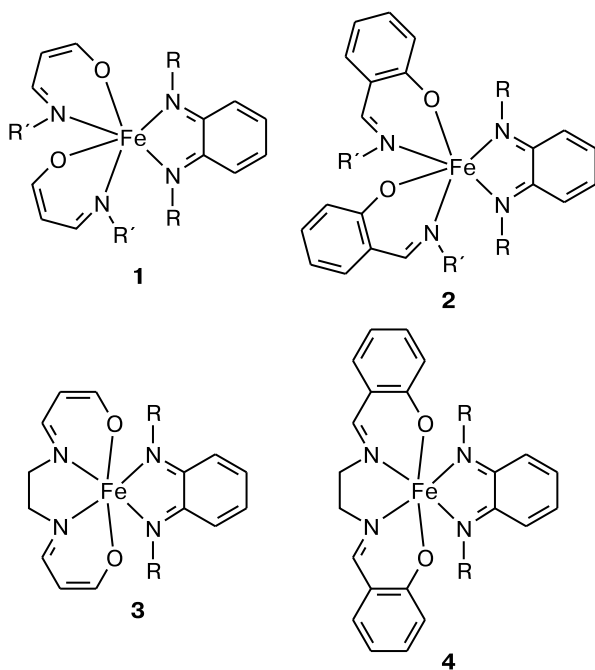
The largest group of the spin-crossover complexes includes Fe^{II} compounds containing iron atoms in octa-

hedral environment of nitrogen atoms,¹³ which provides an appropriate ligand field strength. The next group comprises Fe^{III} complexes with the FeN₄O₂ coordination site^{14,15} and Co^{II} complexes, the latter being most often characterized by pentacoordination of the central metal atom.^{16,17} Recently, spin crossover in hexacoordinate cobalt clathrochelates was reported.^{18,19}

Reactions of iron coordination compounds with *o*-benzoquinone derivatives are widely used to model enzymatic processes catalyzing the oxygenation of catechols to aliphatic acids *via* the cleavage of aromatic rings.^{20–23} A number of iron complexes with redox-active ligands exhibit spin crossover.^{24,25} Exchange interactions between low-spin Fe^{III} atom and iminosemiquinone have been studied in detail;²⁶ iron complexes with *o*-benzoquinones exhibit valence tautomerism.²⁷

In this work, we propose to use adducts of electrically neutral complexes of tetracoordinate Fe^{II} with *o*-diiminobenzoquinones as building blocks for the design of compounds whose magnetic properties are controlled by external factors.

To this end, we quantum chemically modeled a series of adducts **1–4** based on complexes of tetracoordinate iron atom with *o*-diiminobenzoquinones. Since these N-donor ligands are redox-active, complexes based on them can potentially be characterized by two effects accompanied by switching of magnetic properties, namely, SCO¹² and valence tautomerism.²⁸ The complexes studied include iron *bis*-aminovinyl ketonates (**1**) and iron *bis*-salicylaldiminates (**2**) with different substituents at N atoms, as well as their cyclic analogues, namely, *N,N'*-ethylene-*bis*(aminovinylketonato)iron(II) (**3**) and *N,N'*-ethylene-*bis*(salicylaldiminato)iron(II) (**4**).



R = H, Ph; R' = H, Me, Ph

Calculation Procedure

Calculations were carried out within the framework of the density functional theory (DFT) using the Gaussian 09 program,²⁹ a modified B3LYP* functional,³⁰ and the 6-311++G(d,p) extended basis set. Calculations in this approximation correctly reproduce the energy and geometric parameters of the complexes with redox-active ligands^{31–33} and give reliable values of the energy characteristics of the SCO complexes.^{34,35} Stationary points on the potential energy surface (PES) were located by full geometry optimization of the molecular structures with the wave function stability test. All possible isomers were located using a standard Gaussian 09 procedure (Guess=Fragment=N), which allows one to specify the spin states and charges of particular molecular fragments when generating the initial approximation.

Exchange interactions between the unpaired electrons of paramagnetic centers were evaluated using the "broken symmetry" (BS) approach.³⁶ The exchange constant (J/cm^{-1}) was calculated using the Yamaguchi formula.^{37,38} Graphical images of the molecular structures shown in Figs 1–7 were constructed using the ChemCraft program³⁹ for which Cartesian atomic coordinates obtained from quantum chemical calculations served as input parameters.

Results and Discussion

Adducts 1. According to calculations, the stabilization energies of various isomers of adducts **1a–c** (see Table 1 and Fig. 1) fall in the range between 23 and 27 kcal mol⁻¹, thus being indicative of stability of the compounds with respect to decomposition to the starting molecules. Replacement of hydrogens at the diimine N atoms by phenyl groups (R = Ph, see Fig. 2) causes the stabilization energies to decrease by 7–8 kcal mol⁻¹ compared to those calculated for the compounds with R = H (see Table 1). This can be due to steric hindrance produced by the phenyl groups.

An analysis of bond lengths in the redox-active ligand of adducts **1a–c** suggests its semiquinonate form.^{40–42} Therefore, the interaction of iron aminovinyl ketonates with diiminobenzoquinone is accompanied by metal-to-ligand electron transfer and formation of two paramagnetic centers, one on the Fe³⁺ ion and the other on the redox-active ligand in the semiquinonate form. The spin density distribution in the HS form of complex **1a** (see Fig. 3) demonstrates a considerable extent of spin density transfer from the metal ion to the donor atoms of the aminovinyl ketonate ligand.

The calculated spin density on the Fe³⁺ ion is ~4 a.u., being much lower than the value expected for five unpaired electrons. Calculations for the HS forms of adducts **1** using the "broken symmetry" approach predict a strong antiferromagnetic character of exchange interactions in them ($J = -(334–406) \text{ cm}^{-1}$) and stabilization of the state with a spin of 2. Contrary to this, the calculated exchange interaction in the LS forms of adducts **1a–c** is strongly ferromagnetic in character (see Table 1). Therefore, these LS-compounds are expected to

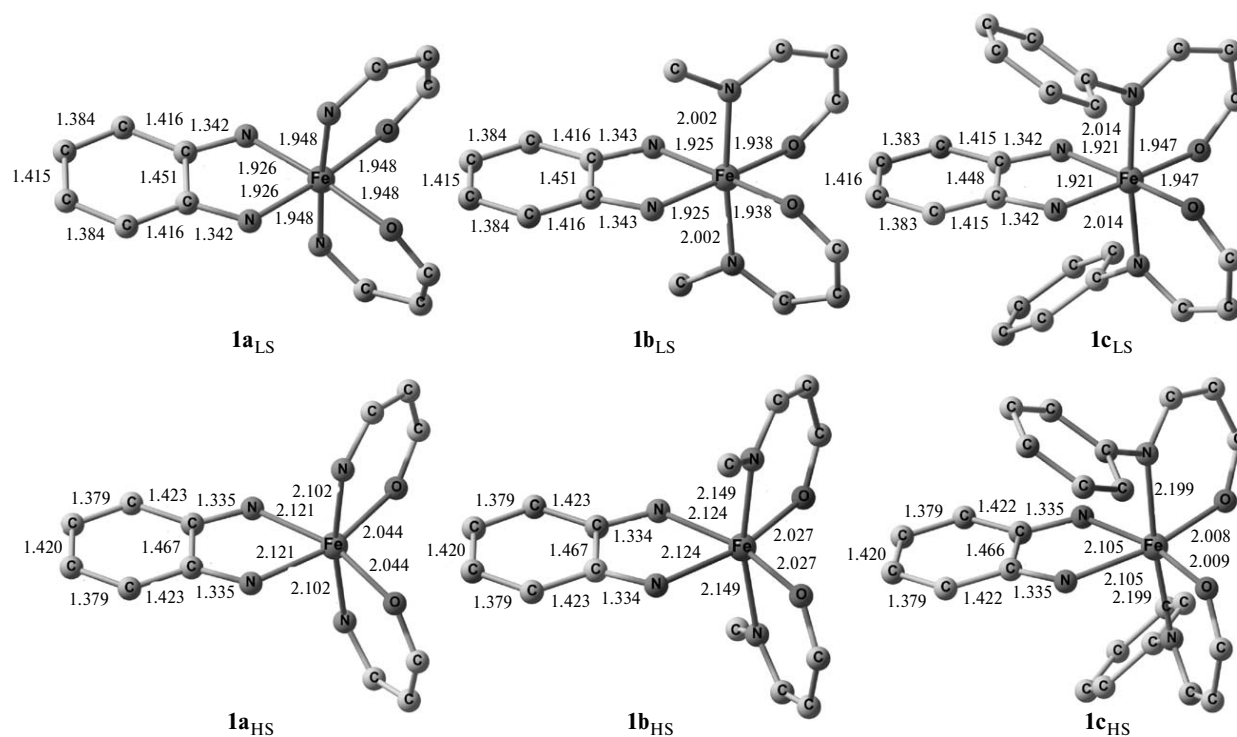


Fig. 1. Geometric parameters of the structures of adducts **1a–c** obtained from DFT/B3LYP*/6-311++G(d,p) calculations. Here and in Figs 2 and 4–7, the bond lengths are given in Å and H atoms are omitted for clarity.

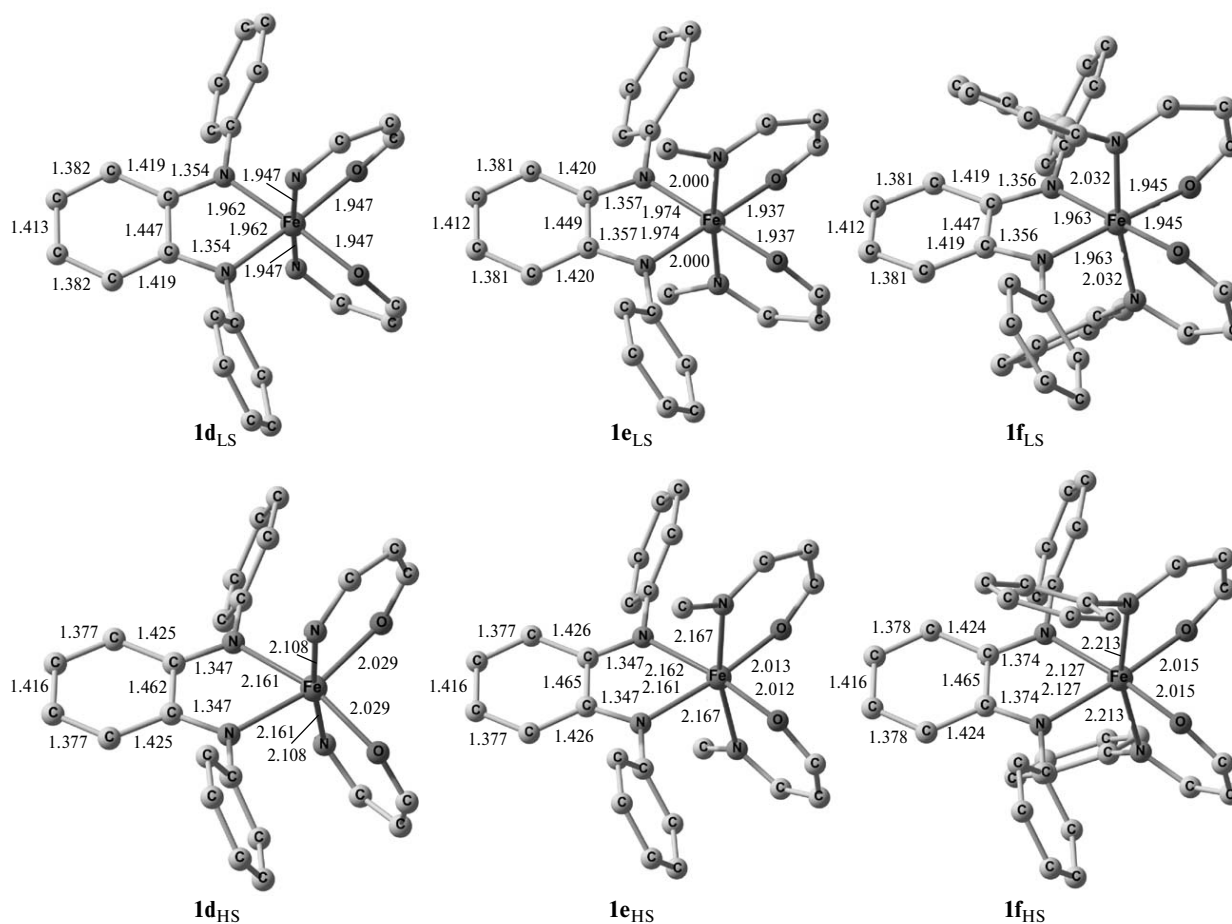


Fig. 2. Geometric parameters of the structures of adducts **1d–f** obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

Table 1. Stabilization energies (E_{st}), energy differences between states calculated with inclusion of exchange interactions (ΔE_{HS-LS}), total energies (E_{tot}), squared spin values (S^2) in the high-spin states, total energies of the BS states (E_{tot}^{BS}), squared spin values (S_{BS}^2) in the BS states, and the exchange constants (J) obtained from DFT/B3LYP*/6-311++G(d,p) calculations of the isomers of adducts **1** and **2**

Structure	R	R'	E_{st}^*	ΔE_{HS-LS}	$-E_{tot}$	S^2	$-E_{tot}^{BS}$	S_{BS}^2	J/cm^{-1}
			kcal mol $^{-1}$		/a.u.		/a.u.		
1a_{LS}	H	H			2098.50291	2.020	2098.50019	1.021	598
1a_{HS}	H	H	25.6	8.0	2098.48212	12.016	2098.49014	6.752	-334
1b_{LS}	H	Me			2177.07132	2.021	2177.06839	1.022	646
1b_{HS}	H	Me	26.6	3.6	2177.05638	12.017	2177.06562	6.727	-383
1c_{LS}	H	Ph			2560.38236	2.021	2560.38039	0.668	319
1c_{HS}	H	Ph	23.7	0.8	2560.37125	12.017	2560.38110	6.689	-406
1d_{LS}	Ph	H			2560.38915	2.019	2560.38699	1.026	476
1d_{HS}	Ph	H	17.3	7.7	2560.37026	12.017	2560.37687	6.763	-276
1e_{LS}	Ph	Me			2638.95379	2.022	2638.95148	1.026	508
1e_{HS}	Ph	Me	15.7	3.5	2638.93865	12.000	2638.94816	6.701	-394
1f_{LS}	Ph	Ph			3022.26294	2.024	3022.26068	1.030	501
1f_{HS}	Ph	Ph	13.5	-1.2	3022.25227	12.017	3022.26484	6.621	-511
2a_{LS}	H	H			2405.66002	2.022	2405.65751	1.020	550
2a_{HS}	H	H	27.9	6.2	2405.64270	12.016	2405.65014	6.773	-311
2b_{LS}	H	Me			2484.23042	2.022	2484.22768	1.022	600
2b_{HS}	H	Me	28.7	1.4	2484.21927	12.016	2484.22821	6.745	-372
2c_{LS}	H	Ph			2867.53951	2.021	2867.53717	1.025	515
2c_{HS}	H	Ph	26.0	-1.5	2867.53252	12.017	2867.54189	6.715	-388
2d_{LS}	Ph	H			2867.54542	2.021	2867.54342	1.027	443
2d_{HS}	Ph	H	19.6	5.3	2867.53063	12.019	2867.53698	6.782	-266
2e_{LS}	Ph	Me			2946.11214	2.023	2946.11001	1.026	467
2e_{HS}	Ph	Me	17.4	1.3	2946.10099	12.017	2946.11003	6.722	-374
2f_{LS}	Ph	Ph			3329.41866	2.000	3329.41680	1.029	420
2f_{HS}	Ph	Ph	15.0	-3.5	3329.41264	12.000	3329.42430	6.658	-479

* Calculated relative to the isolated iron complex and redox-active ligand.

have the properties of paramagnetics in a wide temperature range.

A comparison (see Table 1) of the relative energies of the most stable states of adducts **1** (BS-species for the HS states and structures with ferromagnetic exchange of the unpaired electrons for the LS isomers) discloses a correlation between these energies and the nature of substituents

at N atoms of the aminovinyl ketone ligand. For compound **1a**, the LS form is 8.0 kcal mol $^{-1}$ energetically more preferable than the HS form (BS state), which indicates unfeasibility of thermally induced SCO. In adduct **1b**, H atoms are replaced by methyl groups and ΔE_{HS-LS} decreases to 3.6 kcal mol $^{-1}$. This value falls among typical SCO energies.^{35,43} Phenyl groups at N atoms of the

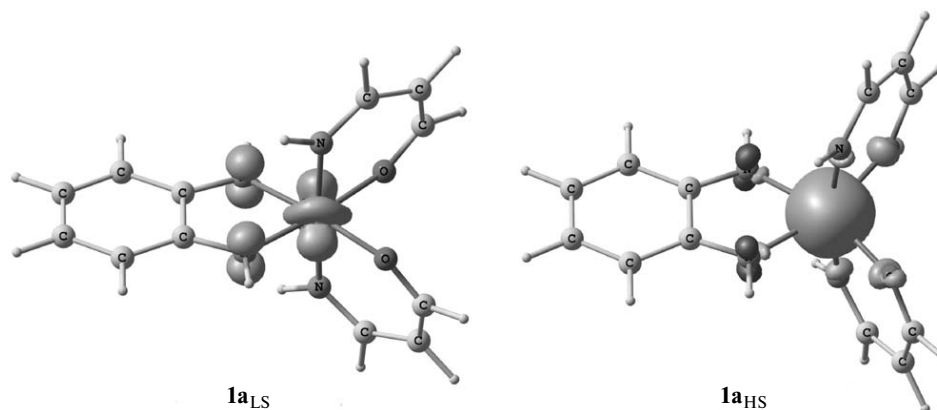


Fig. 3. Spin density distributions in isomers of adduct **1** (R = H, R' = H) obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

aminovinyl ketone ligand ($R' = \text{Ph}$) favor further narrowing of the energy gap $\Delta E_{\text{HS-LS}}$ to a value of $0.8 \text{ kcal mol}^{-1}$ characteristic of SCO.

According to $\Delta E_{\text{HS-LS}}$ calculations for isomers of adducts **1d–f**, SCO in compounds **1d** and **1f** is impossible since in the former case the energy of the LS form is $7.7 \text{ kcal mol}^{-1}$ lower than that of the HS form, the HS structure being more stable in the latter case ($\Delta E_{\text{HS-LS}} = -1.2 \text{ kcal mol}^{-1}$). Only for complex **1e** the energy difference between the isomers is in the characteristic SCO range.

Adducts 2. The results of calculations of adducts **2** based on iron salicylaldehydes (see Figs 4 and 5) demonstrate that annulation of six-membered rings in the aminovinyl ketone ligands has small effect on the geometry of the coordination site in the species being formed. As for adducts **1**, complexation is accompanied by metal-to-ligand electron transfer leading to stabilization of the Fe^{3+} ion and the semiquinonato-dimine form of the redox-active ligand. The absence of isomers containing a Fe^{II} atom points that valence tautomerism in this group of complexes is impossible.

A comparison of the energy differences between the HS and LS isomers of adducts **2** (see Table 1) showed that, irrespective of the type of substituent at the diimine N atoms, thermally induced SCO can be expected only in

the compounds with $R' = \text{Me}$. Phenyl group at the salicylaldehyde N atom stabilizes the HS isomers ($\Delta E_{\text{HS-LS}} = -(1.5\text{--}3.5) \text{ kcal mol}^{-1}$), while the LS forms are more energetically favorable among the complexes with $R' = \text{H}$.

Adducts 3 and 4. An analysis of the results obtained for adducts **3** and **4** showed that, by analogy with compounds **1** and **2**, complexation is accompanied by metal-to-ligand electron transfer (see Figs 6 and 7). The resultant HS and LS isomers contain two paramagnetic centers coupled by exchange interactions. The geometric parameters of the diimine ligand in compounds **3** and **4** differ only slightly from those calculated for complexes **1** and **2**, except for the nonequivalence of the Fe–N bonds originating from the stereochemistry of the tricyclic ligands.

Calculations of exchange interactions in compounds **3** and **4** predict antiferromagnetic bonding of the unpaired electrons in the LS isomers. The J constants are in the range between -470 and -844 cm^{-1} , which should lead to diamagnetism of the isomers containing $\text{Fe}_{\text{LS}}^{3+}$ ions.

To disclose the reasons for antiferromagnetic exchange in the LS isomers of adducts **3** and **4**, the spin density distribution in the BS states was analyzed. The S_{BS}^2 value is $0.6\text{--}0.7$ (Table 2), being much smaller than the value expected for the singlet biradical ($S_{\text{BS}}^2 = 1$). Calculations using a known formula⁴⁴ show that the biradical character of these states is $39\text{--}46\%$.

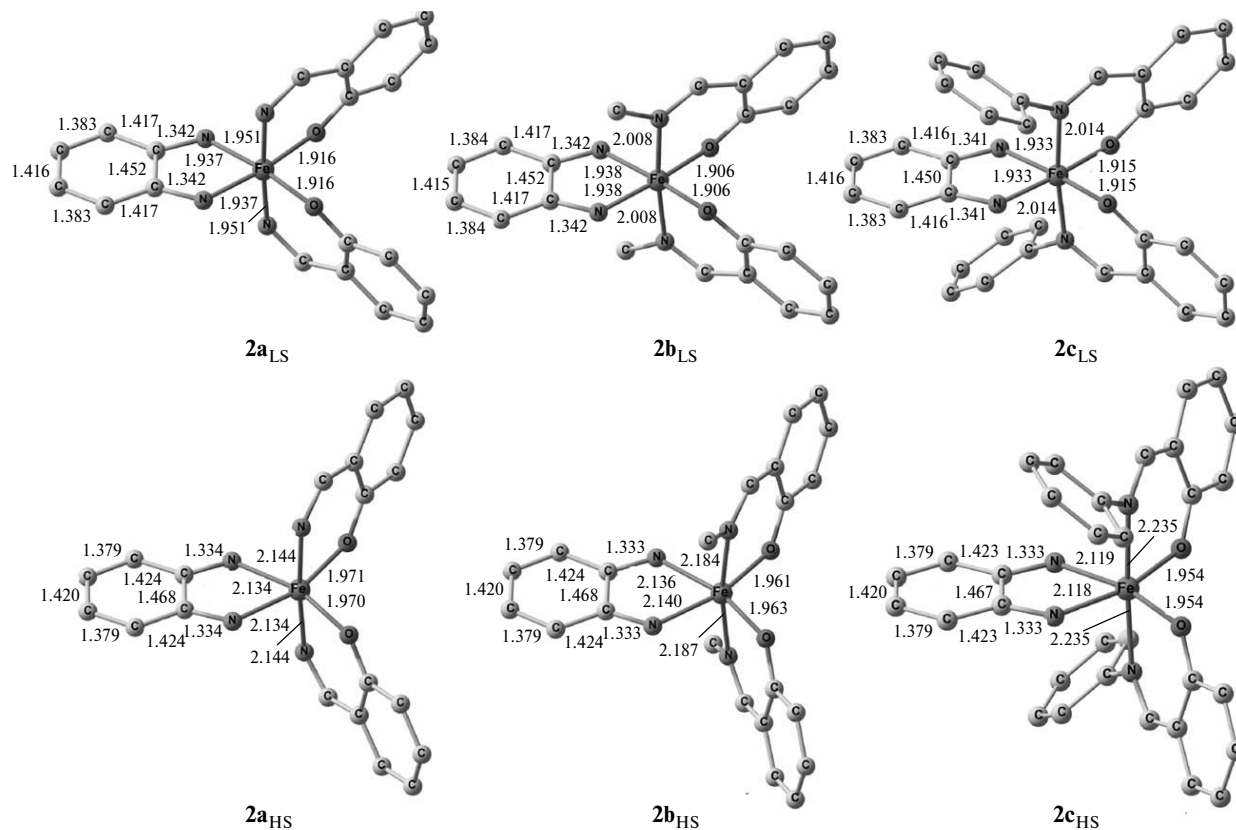


Fig. 4. Geometric parameters of the structures of adducts **2a–c** obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

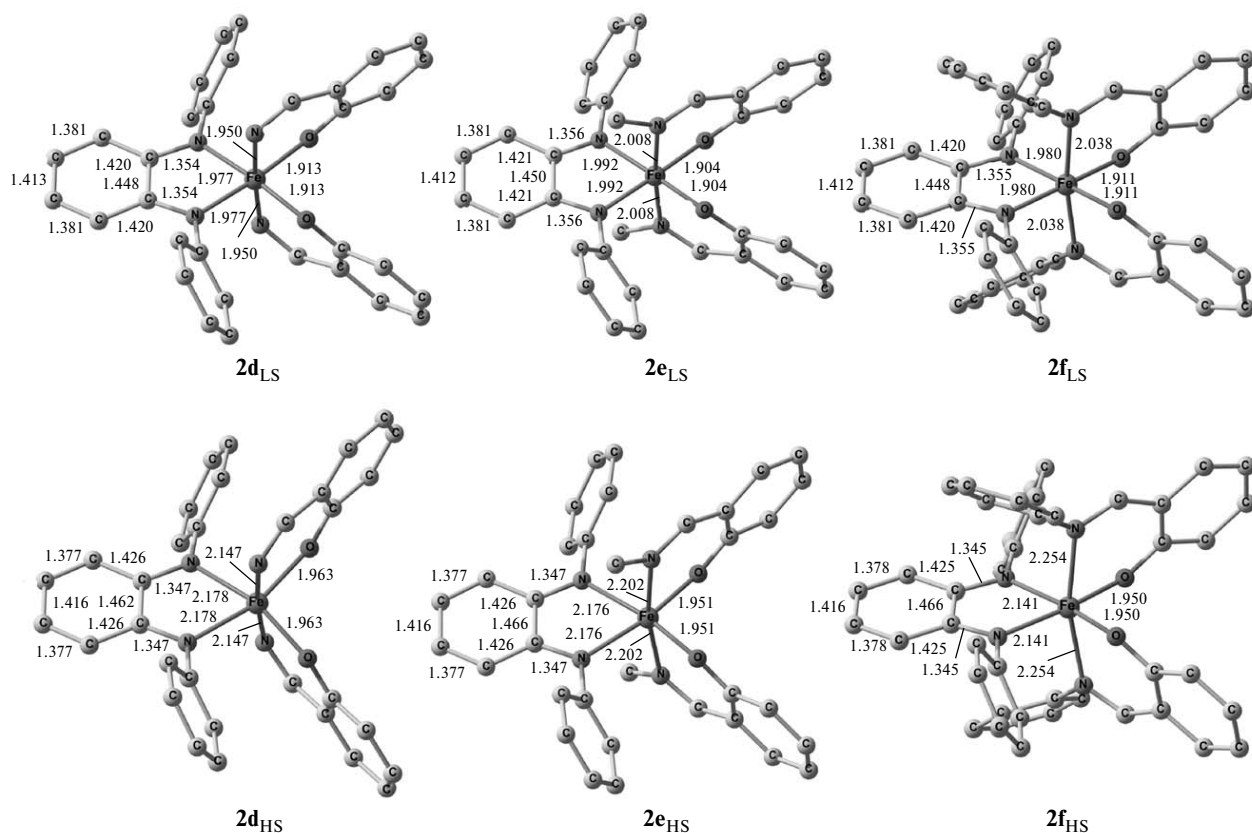


Fig. 5. Geometric parameters of the structures of adducts 2d–f obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

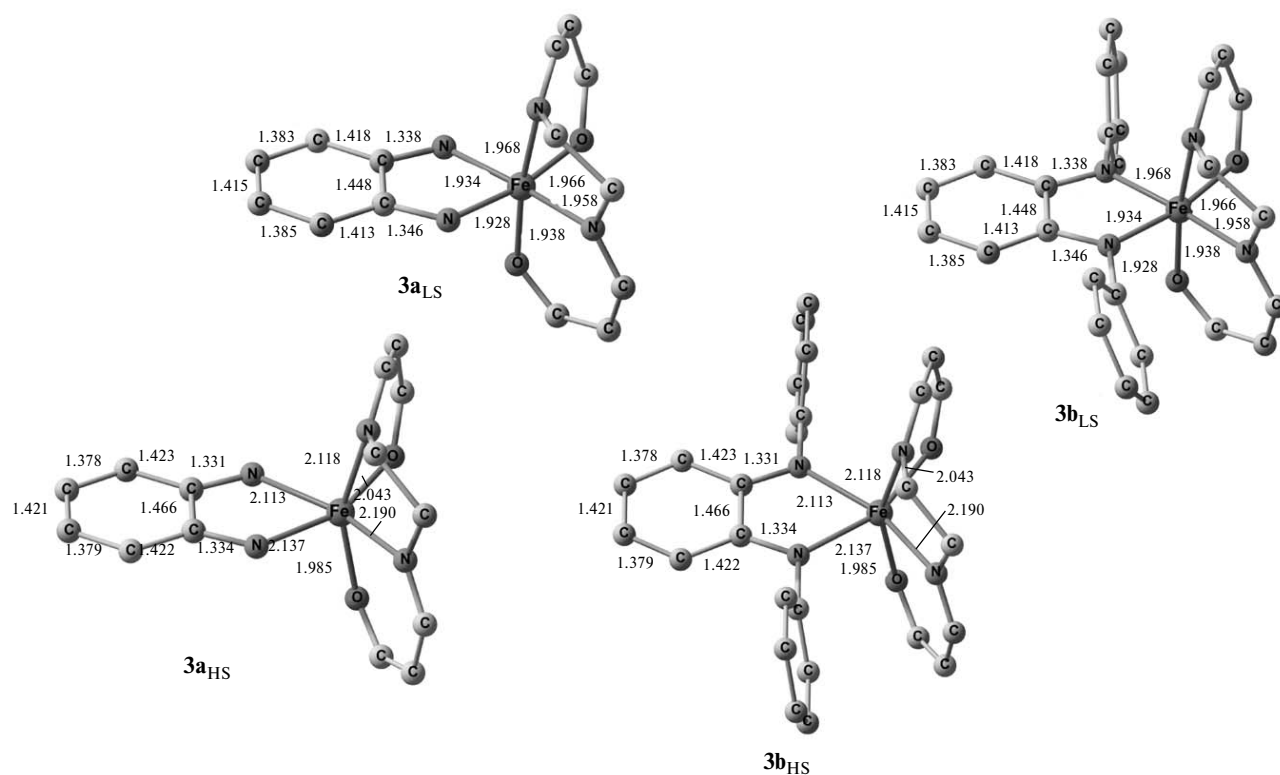


Fig. 6. Geometric parameters of the structures of adducts 3 obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

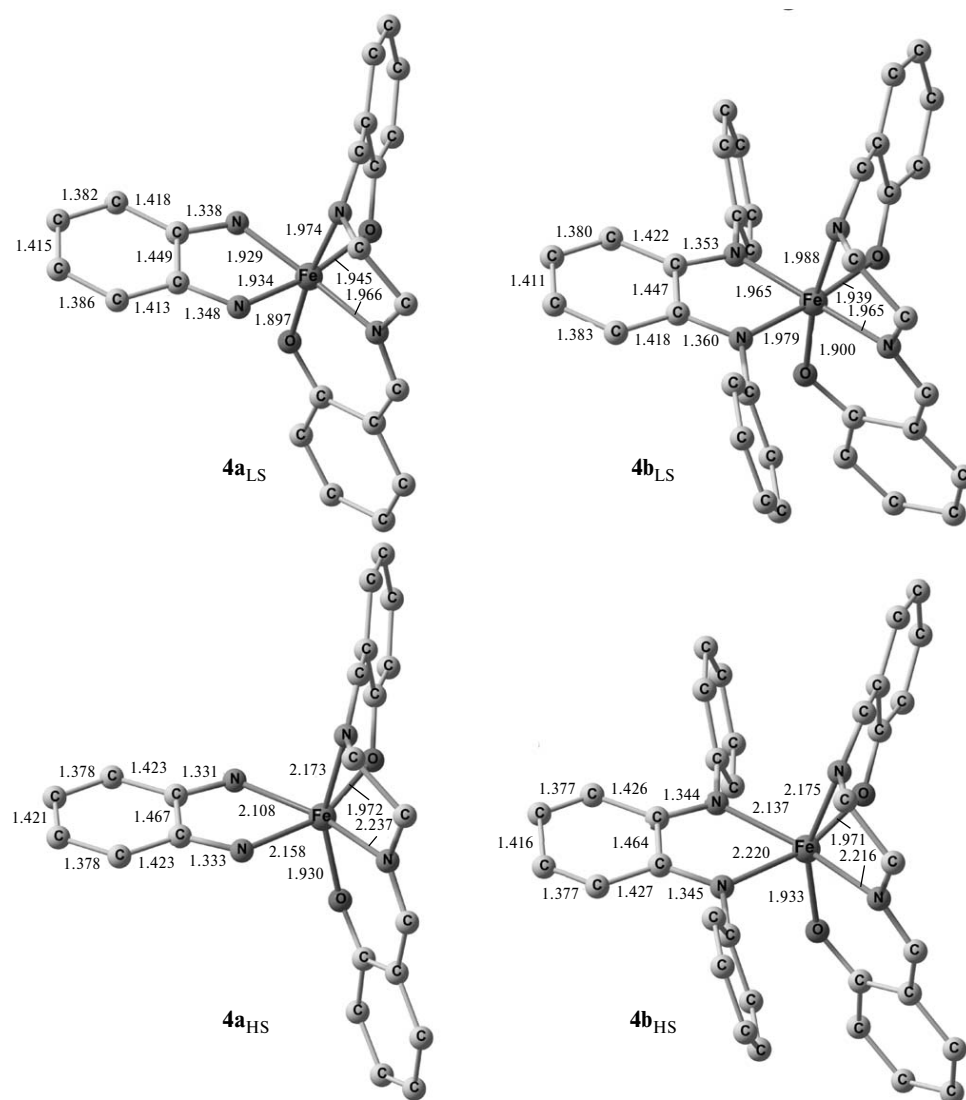


Fig. 7. Geometric parameters of the structures of adducts **4** obtained from DFT/B3LYP*/6-311++G(d,p) calculations.

Table 2. Stabilization energies (E_{st}), energy differences between states calculated with inclusion of exchange interactions (ΔE_{HS-LS}), total energies (E_{tot}), squared spin values (S^2) in the high-spin states, total energies of the BS states (E_{tot}^{BS}), squared spin values (S_{BS}^2) in the BS states, and the exchange constants (J) obtained from DFT/B3LYP*/6-311++G(d,p) calculations of the isomers of adducts **3** and **4**

Structure	R	E_{st}^* kcal mol ⁻¹	ΔE_{HS-LS} kcal mol ⁻¹	$-E_{tot}$ /a.u.	S^2	$-E_{tot}^{BS}$ /a.u.	S_{BS}^2	J/cm^{-1}
3a_{LS}	H			2175.85907	2.022	2175.86442	0.631	-844
3a_{HS}	H	31.7	2.3	2175.85118	12.017	2175.86074	6.732	-397
3b_{LS}	Ph			2637.74121	2.0249	2637.74550	0.668	-694
3b_{HS}	Ph	21.4	0.7	2637.73606	12.019	2637.74438	6.740	-346
4a_{LS}	H			2483.01547	2.024	2483.01953	0.711	-680
4a_{HS}	H	31.9	-0.8	2483.01254	12.018	2483.02074	6.767	-343
4b_{LS}	Ph			2944.89718	2.0245	2944.90004	0.688	-470
4b_{HS}	Ph	21.5	-2.6	2944.89632	12.020	2944.90413	6.766	-326

* Calculated relative to the isolated iron complex and redox-active ligand.

Similarly to the HS isomers of adducts **1** and **2**, all the HS isomers of adducts **3** and **4** are characterized by anti-ferromagnetic exchange interaction between the unpaired electrons localized on the metal ion and the semiquinone. A comparison of the energies of the states corresponding to the HS and LS isomers of adducts **3** and **4** suggests that SCO can occur only in the complexes based on the cyclic aminovinyl ketonates.

Summing up, our DFT/B3LYP*/6-311++G(d,p) study revealed that the formation of adducts of tetracoordinate Fe^{II} complexes with *o*-diiminobenzoquinones is accompanied by electron transfer from the metal ion to the redox-active ligand and transformation of the latter to the semiquinone form. The calculated stabilization energies of adducts **1**–**4** fall in the range from 13 to 32 kcal mol⁻¹, thus indicating thermodynamic stability of the species.

Calculations predict strong exchange interactions between paramagnetic centers localized on the Fe³⁺ ion and on the semiquinone fragment. Ferromagnetic exchange is predicted for the LS structures of adducts **1** and **2** based on *bis*-chelates, whereas antiferromagnetic exchange is predicted for the HS structures. Complexes with tetradentate ligands **3** and **4** are characterized by antiferromagnetic exchange interactions for both types of isomers.

Isomers containing Fe^{II} atoms do not exist (no corresponding minima were located on the PES). Therefore, valence tautomerism in this type of compounds is impossible. By varying substituents in the complexes of tetracoordinate iron and *o*-diiminobenzoquinone we succeeded to locate coordination compounds whose HS forms lie 1–4 kcal mol⁻¹ higher than the corresponding LS ones on the energy scale; this allows one to expect thermally induced SCO. The energy difference necessary for the effect to occur is achieved for the complexes containing methyl group at N atoms of the initial *bis*-chelate and for adducts **3**.

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