

Dual Magnetic Behavior of Co(II) and Fe(II) Bis(chelate) Adducts with Di-*o*-Diiminobenzoquinone: Quantum Chemical Modeling

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Abstract—Computational modeling (DFT UB3LYP*/6-311++G(d,p)) of electroneutral binuclear 2 : 1 adducts of cobalt and iron bis(chelates) with *N*-phenyl-di-*o*-diiminobenzoquinone bearing the dimethylene linker is performed. The geometries of all electromers of the complexes are determined, and their stabilization energies and exchange interaction parameters are calculated. The magnetic properties of the compounds under study are determined by the metal nature: the cobalt diketonate adducts undergo one- and two-step valence tautomeric rearrangements, while the mixed-ligand iron complexes are capable of demonstrating spin crossover. The calculation results make it possible to regard the studied adducts as the basis for designing molecular switches and spin qubits.

Keywords: transition metal bis(chelates), di-*o*-diiminobenzoquinones, magnetic properties, spin crossover, valence tautomerism, quantum chemical modeling

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INTRODUCTION

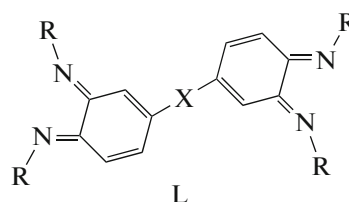
Molecular magnetism [1], lying at the intersection of chemistry, physics, and materials science, is an actively developed area of the modern science. Compounds with this property can serve as a basis for designing devices of molecular electronics and spintronics [2], temperature and pressure sensors [3], a new generation of contrast agents for magnetic resonance tomography [4], and switchable organic light-emitting diodes [5].

The main mechanisms of magnetic bistability of transition metal coordination compounds are spin crossover, being the electron rearrangement inside the valence shell of the metal between its low- and high-spin states [6], and valence tautomerism, being the reversible electron transfer between the metal and redox-active ligand [7]. The former effect is met most frequently in the hexacoordinated iron complexes with nitrogen-centered ligands having an appropriate strength of the field [8, 9], while the latter is manifested in the cobalt coordination compounds with *o*-quinones and their imino derivatives [10, 11].

An approach to the preparation of magnetically active compounds aimed at searching for electroneutral adducts of tetracoordinated transition metal complexes and a redox-active ligand has been proposed recently [12, 13]. According to the later quantum chemical calculations [14–17], the binuclear coordination compounds built as 2 : 1 adducts of cobalt and iron bis(chelates) with di-*o*-diquinones are also capa-

ble of demonstrating two-step mechanisms of switching spin states, which makes it possible to consider them as candidates for the development of molecular switches and spin quantum bits.

In order to search for tetradentate ligands suitable for the construction of binuclear complexes, which are potentially capable of changing the magnetic properties due to spin transitions, we considered di-*o*-diiminobenzoquinones (L), nitrogen-centered redox-active ligands, whose oxygen analogs were well studied [18–21]. These organic molecules can form adducts with cobalt and iron bis(chelates).



R = H, Ph;

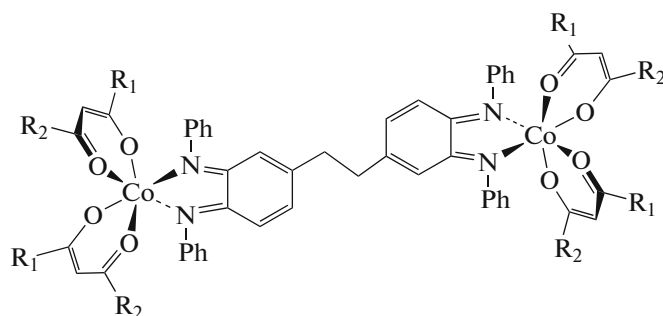
X = none, HC=HC,

H₂C–CH₂, piperazindiyli

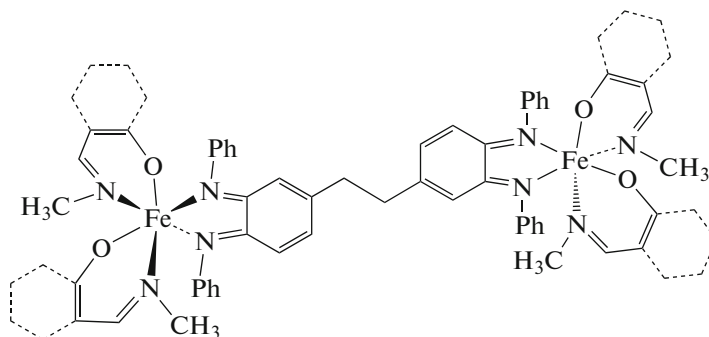
This work is devoted to the computational design of binuclear coordination compounds of transition metals, whose magnetic properties can be controlled by two-step valence tautomerism and spin crossover rearrangements. It has previously been shown [14] that di-*o*-diquinone with the dimethy-

lene linker ($X = \text{H}_2\text{C}-\text{CH}_2$), which provides weak exchange interactions between paramagnetic centers, is a promising ligand for the structural design of coordination compounds manifesting the properties of qubits, logical units of quantum computers [22]. According to the calculations [23–26], the variation of substituents in the bis(chelate) fragments of the mixed-ligand complexes of cobalt diketonates with diimine ligands allows one to find molecules satisfying the conditions of valence tautomerism rearrangements [27]. It is revealed by the quantum chemical modeling of the mononuclear adducts of the iron azomethine complexes

with *o*-diiminobenzoquinones [28] that the necessary characteristics for spin crossover to occur are achieved in the compounds containing the methyl group at the nitrogen atoms of the aminovinylketone or salicylaldehyde ligands. Based on the previously obtained results, we performed the computational modeling of binuclear mixed-ligand complexes of cobalt diketonates **I** ($R_1, R_2 = \text{CH}_3, \text{CF}_3$), iron aminovinylketonates **II**, and iron salicylaldiminates **III** with synthetically available *N*-phenyl-di-*o*-diiminobenzoquinone bearing the dimethylene linker.



I: $R_1, R_2 = \text{CH}_3, \text{CF}_3$



(II), (III)

CALCULATION PROCEDURE

The calculations were performed using the Gaussian 09 program [29] by the density functional theory (DFT) with the UB3LYP* modified functional [30] and the 6-311++G(d,p) extended basis set. It has previously been shown that the chosen approach correctly reproduces the geometric characteristics of the coordination compounds with the redox-active ligands [31–33] and reliably describes the energetic parameters of the complexes having spin crossover [34, 35]. Stationary points were localized on the potential energy surface (PES) by the full geometry optimization of the molecular structures checking the DFT stability of the wave function. The exchange interaction parameters (J, cm^{-1}) were determined by the calcula-

tion of all possible spin states of the isomers in the framework of the broken symmetry (BS) formalism [36] using the generalized spin projection method proposed by Yamaguchi [37]. The graphical images of the molecular structures presented in Figs. 1–4 were obtained using the ChemCraft program [38].

RESULTS AND DISCUSSION

Adducts of Co(II) bis(chelates). The spin density distribution in the isomeric (electromeric [39]) species of adducts **I** ($R_1, R_2 = \text{CH}_3, \text{CF}_3$) presented in Fig. 1 is similar to that found earlier in the binuclear cobalt complexes with di-*o*-diquinones [14, 15, 17]. In the structures on the triplet PES including three-charged

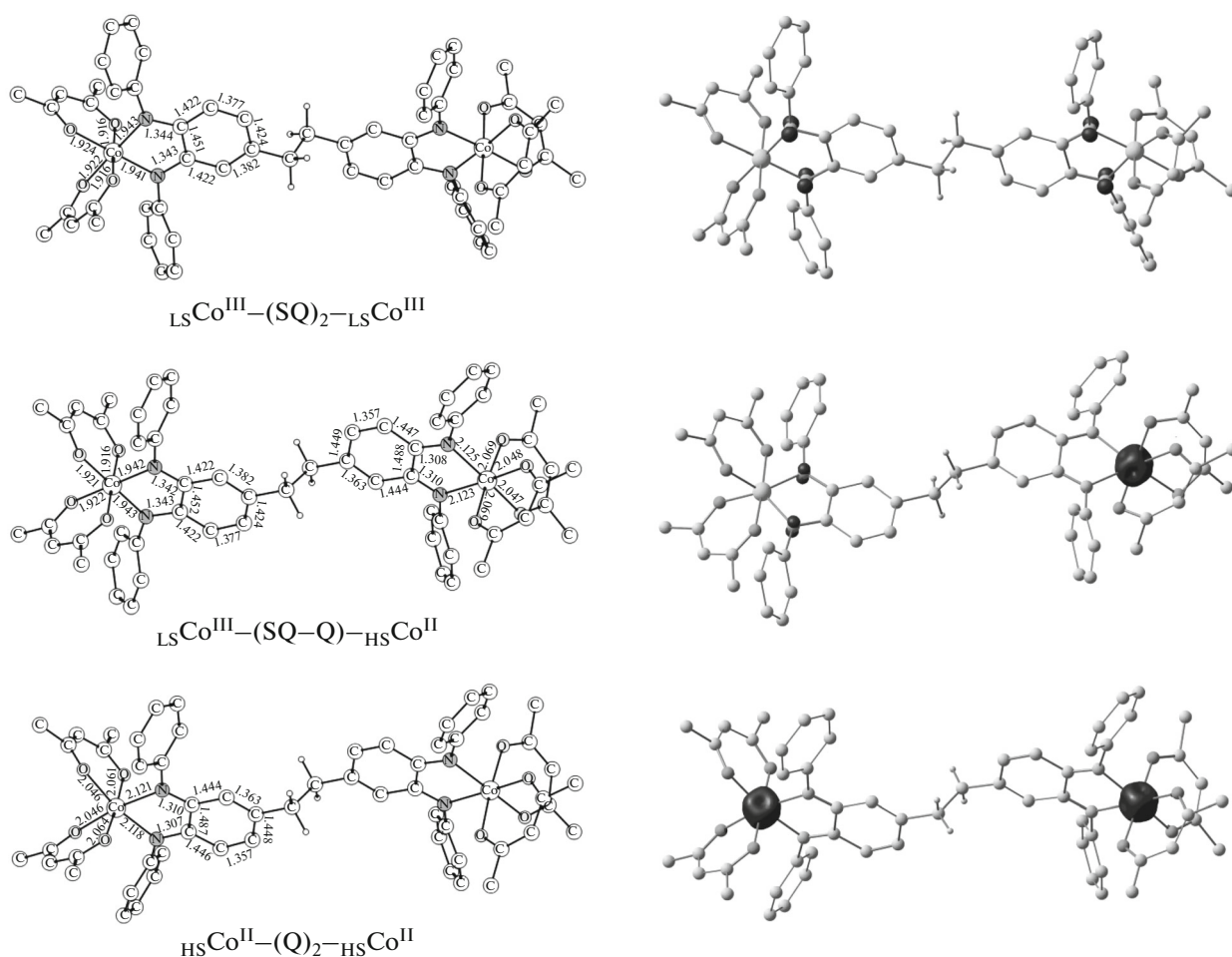


Fig. 1. Geometric characteristics and spin density distribution in the isomeric species of adduct I ($R_1, R_2 = CH_3$) calculated by the DFT UB3LYP*/6-311++G(d,p) method. Hereinafter, bond lengths are given in Å and hydrogen atoms, except for those in the dimethylene linker, are omitted for clarity.

low-spin cobalt ions, the spin density is localized on the radical-containing fragments between which a weak antiferromagnetic interaction is expected (Table 1). The transfer of an electron from the diimine ligand to one of the metals resulting in the transition of the latter to the high-spin state is predicted for the isomers to which minima on the quintet PES correspond. The calculation of the magnetic properties of these species of adducts indicates the ferromagnetic exchange between unpaired electrons of the cobalt ion and redox-active fragment (Table 1, Fig. 1). No exchange interactions are observed in the structures on the septet PES characterized by the presence of unpaired electrons on the cobalt ions only.

According to the calculations, the low-spin ($S = 2/2$) structure $LSCo^{III}-(SQ)_2-LSCo^{III}$ (SQ is the radical-anionic semiquinone species of the redox-active fragment of the diimine ligand) corresponds to the ground state of the adduct with cobalt bis(acetylacetonates). Therefore, complex formation is accompanied by the electron transfer from the metal ions to the

ligand. The parameter of exchange interactions between unpaired electrons localized on the diimine moieties of the tetradentate ligand is -18 cm^{-1} , indicating paramagnetism of complex I ($R_1, R_2 = CH_3$) in a wide temperature range. The calculated difference in energies (see Table 1) between the structure with the intermediate ($S = 4/2$) spin state and the low-spin isomer ($S = 2/2$) is in the range of experimentally determined values for the cobalt complexes with valence tautomerism [40, 41], which allows one to expect the one-step redox-isomeric rearrangement between electromers $LSCo^{III}-(SQ)_2-LSCo^{III}$ and $LSCo^{III}-(SQ-Q)-HSCo^{II}$ (Q is the electroneutral quinone species of the redox-active fragment of the tetradentate ligand). The destabilization of the high-spin species $HSCo^{II}-(Q)_2-HSCo^{II}$ ($S = 6/2$) relative to the ground state by 19.3 kcal/mol indicates that it cannot be achieved under the thermal conditions.

The introduction of the electron-withdrawing trifluoromethyl substituents into the diketone ligands

Table 1. Spin (S), stabilization energy (E_{st}), relative energy (ΔE), and exchange interaction parameter (J) in the isomeric species of adducts **I** ($R_1, R_2 = \text{CH}_3, \text{CF}_3$) calculated by the DFT B3LYP*/6-311++G(d,p) method

Structure	S	E_{st}^*	ΔE	J, cm^{-1}
		kcal/mol		
$R_1 = R_2 = \text{CH}_3$				
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ})_2-{}_{\text{LS}}\text{Co}^{\text{III}}$	2/2	50.4	0.0	-18
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ}-\text{Q})-{}_{\text{HS}}\text{Co}^{\text{II}}$	4/2	41.7	8.7	2
${}_{\text{HS}}\text{Co}^{\text{II}}-(\text{Q})_2-{}_{\text{HS}}\text{Co}^{\text{II}}$	6/2	31.1	19.3	0
$R_1 = \text{CH}_3, R_2 = \text{CF}_3$				
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ})_2-{}_{\text{LS}}\text{Co}^{\text{III}}$	2/2	54.5	0.0	-19
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ}-\text{Q})-{}_{\text{HS}}\text{Co}^{\text{II}}$	4/2	51.7	2.7	1
${}_{\text{HS}}\text{Co}^{\text{II}}-(\text{Q})_2-{}_{\text{HS}}\text{Co}^{\text{II}}$	6/2	46.8	7.7	0
$R_1 = R_2 = \text{CF}_3$				
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ})_2-{}_{\text{LS}}\text{Co}^{\text{III}}$	2/2	61.2	0.0	-19
${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ}-\text{Q})-{}_{\text{HS}}\text{Co}^{\text{II}}$	4/2	64.6	-3.4	1
${}_{\text{HS}}\text{Co}^{\text{II}}-(\text{Q})_2-{}_{\text{HS}}\text{Co}^{\text{II}}$	6/2	66.5	-5.3	0

* The stabilization energies were calculated relative to isolated molecules of the metal bis(chelates) and redox-active ligand.

(Fig. 2) decreases differences in energy between the electromeric species: the relative energies of electron-excited isomers ${}_{\text{LS}}\text{Co}^{\text{III}}-(\text{SQ}-\text{Q})-{}_{\text{HS}}\text{Co}^{\text{II}}$ and ${}_{\text{HS}}\text{Co}^{\text{II}}-(\text{Q})_2-{}_{\text{HS}}\text{Co}^{\text{II}}$ of mixed-ligand complex **I** ($R_1 = \text{CH}_3, R_2 = \text{CF}_3$) are 2.7 and 7.7 kcal/mol, respectively. This indicates the possibility of two consecutive intramolecular electron transitions to occur. The high stabilization energy ($E_{st} = 46.8$ kcal/mol), predicted two-step valence tautomerism, and weak exchange interactions between paramagnetic centers ($<|20| \text{cm}^{-1}$) make it possible to regard the adduct of cobalt bis(trifluoroacetylacetonates) with *N*-phenyl-substituted di-*o*-diiminobenzoquinone as a candidate for the development of spin qubits.

The inversion of the relative energies of the electromers is observed on going to the hexafluoroacetylacetonate systems: the structures including the high-spin two-charge cobalt ions turn out to be the ground state (Table 1), which prevents thermally initiated intramolecular electron transfer in adduct **I** ($R_1 = R_2 = \text{CF}_3$) to occur.

Adducts of Fe(II) bis(chelates). As follows from the calculation results for the iron complexes, adduct formation is accompanied by the oxidation of the metal ions to the trivalent state and transition of the redox-active ligand to the dianion–diradical form. No isomers including divalent iron ions were observed (the minima on the PES corresponding to these structures

are absent), which is consistent with the results of the previous computational modeling of the mononuclear adducts of iron bis(chelates) with the diimine ligands [28] and indicates that valence tautomerism does not take place in adducts **II** and **III**.

The structures ${}_{\text{LS}}\text{Fe}^{\text{III}}-(\text{SQ})_2-{}_{\text{LS}}\text{Fe}^{\text{III}}$ including low-spin iron ions Fe^{3+} correspond to the ground state of the considered mixed-ligand iron complexes (Figs. 3 and 4). The electromers with an intermediate spin ${}_{\text{LS}}\text{Fe}^{\text{III}}-(\text{SQ})_2-{}_{\text{HS}}\text{Fe}^{\text{III}}$ in which the metal ions have different spin states are the next in energy. The least favorable structures are presented by the high-spin species ${}_{\text{HS}}\text{Fe}^{\text{III}}-(\text{SQ})_2-{}_{\text{HS}}\text{Fe}^{\text{III}}$. For the estimation of exchange interactions in compounds **II** and **III** containing four paramagnetic centers, all BS states were determined using the procedure (Guess = Fragment = N) that makes it possible to attribute the spin state and charge to particular moieties of the molecule at the stage of initial approximation generation. The exchange interaction constants (calculated using the generalized spin projection method [37]) are presented in Table 2. Spins of unpaired electrons of the low-spin metal ion and adjacent redox-active fragment are coupled ferromagnetically ($J = 450\text{--}520 \text{cm}^{-1}$), while the exchange interactions between the high-spin iron ion and diimine moiety are antiferromagnetic ($J \sim -420 \text{cm}^{-1}$). Regardless of the spin state of the metal, the paramagnetic centers $\text{Fe}^{\text{III}}-\text{SQ}$ and $\text{Fe}^{\text{III}}-$

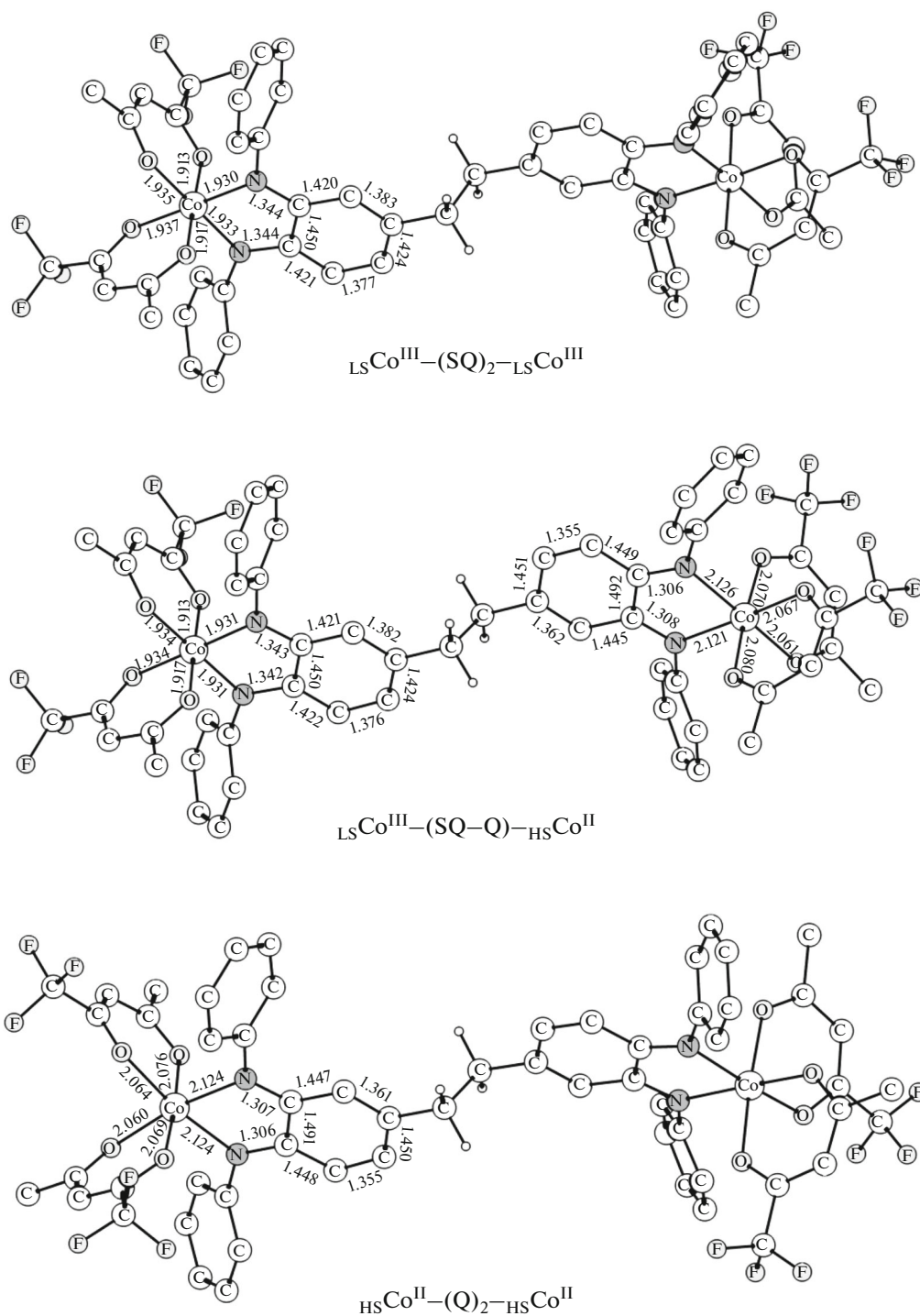


Fig. 2. Geometric characteristics of the isomeric species of adduct I ($R_1 = CH_3$, $R_2 = CF_3$) calculated by the DFT UB3LYP*/6-311++G(d,p) method.

SQ separated by the dimethylene linker do not almost interact.

According to the calculations, the differences in energies between the electromeric species of adduct II (3.7 and 4.8 kcal/mol) are in the range of values at

which spin crossover takes place [35, 42], which allows one to expect that the thermally induced two-step spin transition would occur. The calculated energetic and magnetic characteristics suggest that the mixed-ligand complex of iron *N*-methylaminovinylketonates with

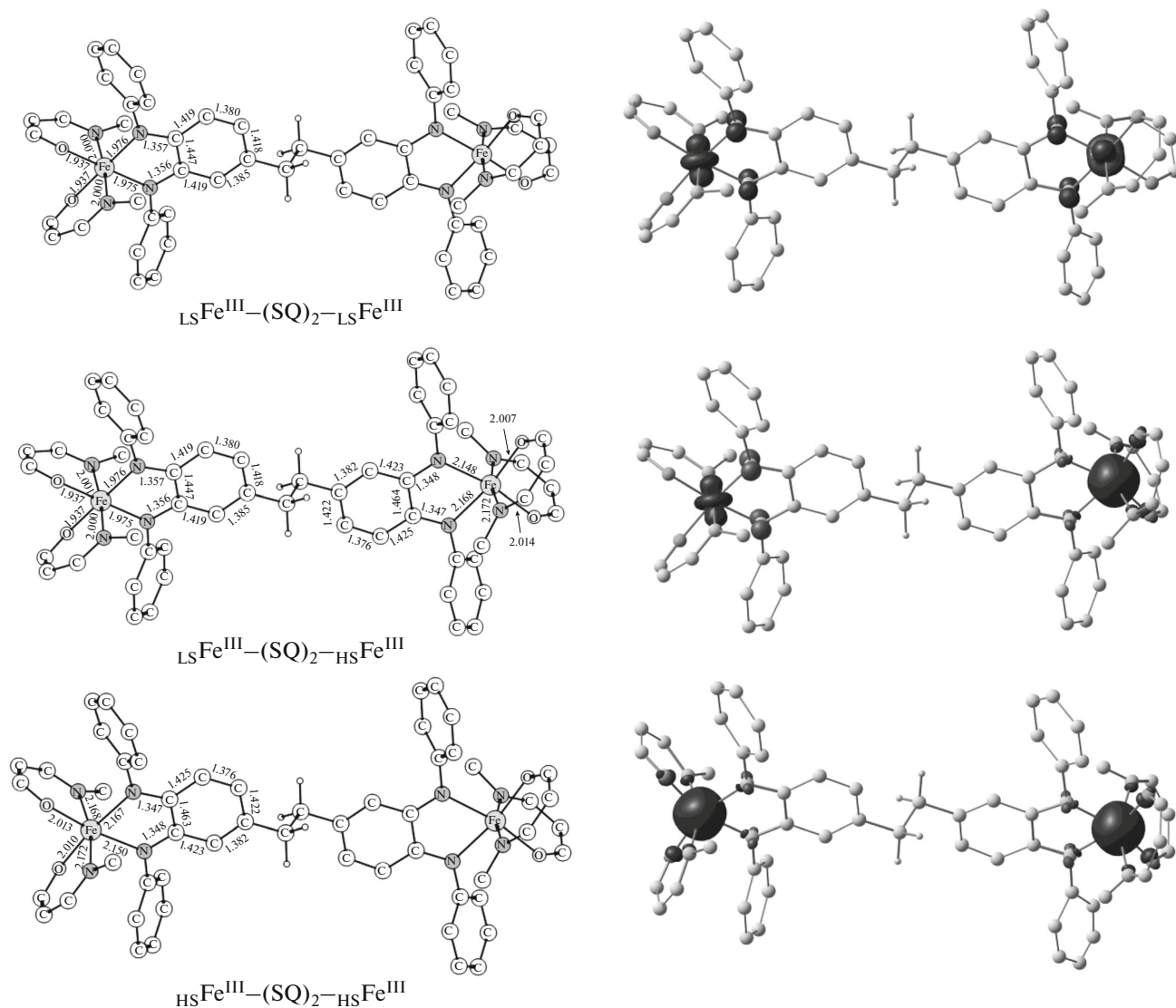


Fig. 3. Geometric characteristics and spin density distribution in the isomeric species of adduct **II** calculated by the DFT UB3LYP*/6-311++G(d,p) method.

N-phenyl-di-*o*-diiminobenzoquinone can manifest the properties of spin qubit.

A decrease in the difference in energies between the electromeric species is observed on going to the adducts of iron bis(salicylaldiminates): the isomer with the intermediate spin state $LSFe^{III}-(SQ)_2-HSFe^{III}$ and high-spin structure $HSFe^{III}-(SQ)_2-HSFe^{III}$ are destabilized relative to the ground state $LSFe^{III}-(SQ)_2-LSFe^{III}$ by 1.2 and 2.1 kcal/mol, respectively. The values obtained for the exchange interaction constants (Table 2) indicate an insignificant influence of annelation of the six-membered ring to the azomethine ligand on the magnetic characteristics of the considered systems. Thermally initiated two-step spin

crossover and paramagnetism of all electromers make it possible to regard compound **III** as a candidate for spin qubits.

To conclude, the results of the performed DFT UB3LYP*/6-311++G(d,p) calculations show the potential ability of the adducts of transition metal bis(chelates) with *N*-phenyl-di-*o*-diiminobenzoquinone to manifest two effects: spin crossover in the iron compounds and valence tautomerism in the cobalt complexes. The spin transitions in compounds **I–III** proceed stepwise favoring the improvement of the key characteristic of spin qubits: quantum entanglement. The predicted energetic and magnetic properties of adducts based on di-*o*-diiminobenzoquinone make it

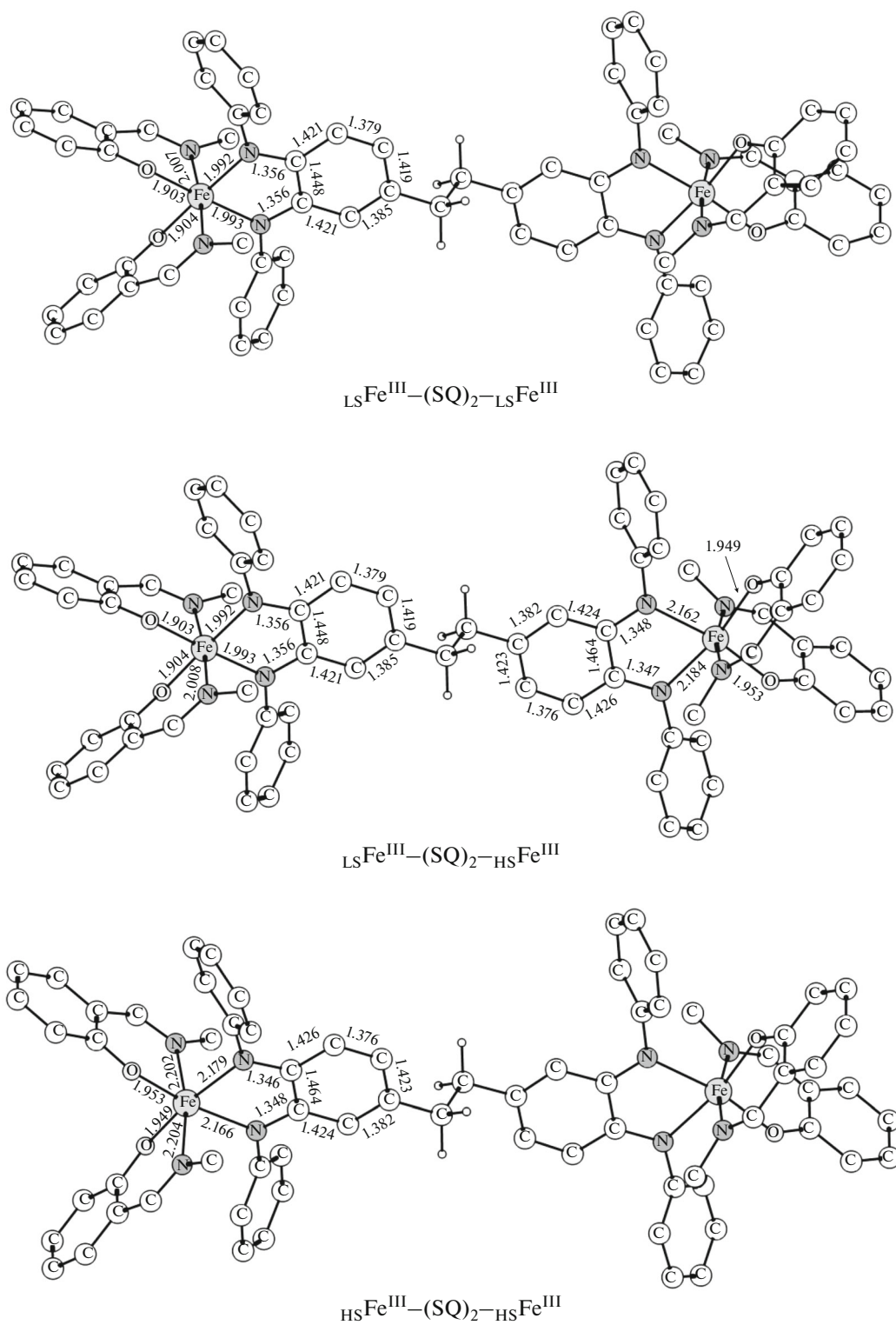


Fig. 4. Geometric characteristics and spin density distribution in the isomeric species of adduct **III** calculated by the DFT UB3LYP*/6-311++G(d,p) method.

Table 2. Spin (S), stabilization energy (E_{st}), relative energy (ΔE), and exchange interaction parameter (J^*) in the isomeric species of adducts **II** and **III** calculated by the DFT B3LYP*/6-311++G(d,p) method

Structure	S	E_{st}	ΔE	J_{SQ-SQ}	$J_{(LS^{Fe-SQ})}$	$J_{(HS^{Fe-SQ})}$
		kcal/mol		cm ⁻¹		
Adduct II						
LSFe ^{III} –(SQ) ₂ –LSFe ^{III}	4/2	37.2	0.0	–6	516	
LSFe ^{III} –(SQ) ₂ –HSFe ^{III}	8/2	33.5	3.7	–12	467	–412
HSFe ^{III} –(SQ) ₂ –HSFe ^{III}	12/2	32.4	4.8	–10		–415
Adduct III						
LSFe ^{III} –(SQ) ₂ –LSFe ^{III}	4/2	36.0	0.0	–8	510	
LSFe ^{III} –(SQ) ₂ –HSFe ^{III}	8/2	34.8	1.2	–15	454	–421
HSFe ^{III} –(SQ) ₂ –HSFe ^{III}	12/2	33.9	2.1	–9		–426

* The exchange interactions between the iron ions and between the iron ion and redox-active fragment separated by the dimethylene linker are equal to zero and omitted from the table.

possible to regard them as candidates for designing devices for molecular electronics and spintronics.

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