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The authors congratulate Academician I.L. Eremenko with a 70th birthday

Computer Simulation of the Structure and Magnetic Properties of Cobalt Complexes with *N*-Substituted Pyridinophanes and Radical-Functionalized *o*-Benzoquinones

V. I. Minkin[a], **A. A. Starikova**[a, *], **M. G. Chegerev**[a], **and A. G. Starikov**[a]

[a] *Institute of Physical and Organic Chemistry, Southern Federal Univertsity, Rostov-on-Don, Russia*

**e-mail: alstar@ipoc.sfedu.ru*

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Abstract—The structure and energy and magnetic characteristics of mononuclear cobalt complex with *N*,*N*'-dialkyl-2,11-diaza[3.3]-(2,6)pyridinophanes and *o*-benzoquinone ligands containing stable radicals (nitronyl nitroxide and TEMPO) were studied by the density functional theory (DFT UTPSSh/6-311++G(d,p)). It was shown that the stability of electromeric forms of complexes and, hence, the possibility of implementing the magnetic bistability mechanisms (spin-crossover and valence tautomerism) can be controlled by varying alkyl substituents at the tetraazamacrocycle nitrogen atoms. The nature of the radical group determines the strength of exchange interactions in which it participates, but does not affect the exchange in the redox-active moiety.

Keywords: cobalt, 2,11-diaza[3.3]-(2,6)pyridinophanes, *o*-benzoquinone, stable radicals, magnetic properties, electronic structure

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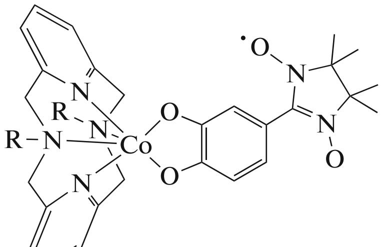
INTRODUCTION

The search for open-shell transition metal complexes exhibiting one of the most significant types of electronic bistability, variability of magnetic properties, is a promising area of chemistry and materials science. These magnetically active compounds could find applications for the design of molecular switches, molecular magnets, memory devices, and spin qubits. [1–9]. The most frequent mechanisms of the change of magnetic characteristics on exposure to external stimuli (temperature, light, pressure, electromagnetic field, etc.) include spin crossover (SCO), caused by an electronic rearrangement between low-spin and high-spin states within the metal valence shell [4, 10], and valence tautomerism (VT), reversible intramolecular electron transfer involving the transition metal ion and a coordinated redox-active ligand [11]. The SCO has been extensively studied for iron complexes [12, 13], but it is also encountered in cobalt compounds [14], while VT has been studied in detail for cobalt systems with o-benzoquinones (dioxolenes) [15–18].

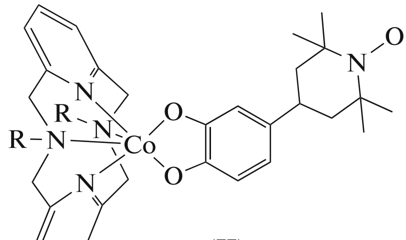
A series of publications is devoted to the synthesis and investigation of cationic transition metal complexes containing one redox-active ligand and a tetradentate macrocyclic nitrogen-containing base [19–31]. This structural motif has been efficiently utilized to produce binuclear magnetically active compounds [32–40]. Systems constructed in this way draw attention because of their ability to undergo both VT [19, 21–28] and SCO [30, 31], depending on the nature of the tetraazamacrocyclic ligand. A recent theoretical and experimental study of a series of *o*-benzoquinone cobalt complexes with *N*,*N*'-dialkyl-2,11-diaza[3.3]-(2,6)pyridinophanes (pyridinophanes) demonstrated that the possibility and the mechanism of rearrangements changing the spin state can be controlled by substituents at the macrocycle nitrogen atoms [41–43].

The metal complexes with *o*-quinones functionalized by radicals attract particular attention as they contain three spin carriers, the metal ion, the radical anion semiquinone (SQ) form of the ligand, and the paramagnetic substituent. First-row transition metal complexes with *o*-quinone ligands containing a nitronyl nitroxide radical, bound to the dioxolene ring either directly or via bridging groups, have been reported [44–48]. There are studies dealing with heterospin manganese, cobalt, nickel, and copper complexes with two redox-active ligands containing a paramagnetic group in the auxiliary nitrogen-containing base [49–52] and cobalt compounds incorporating 3,6-di-*tert*-butyl-*o*-benzoquinone ligands and 1,3,5-triphenylformazanate anion [53]. The successful synthesis and structure determination of iron(III) complex with catechol (Cat) containing nitronyl nitroxide substituent and tris(2-pyridylmethyl)amine ligand [48] as well as the diversity of the chemistry of stable radicals [54, 55] open up wide prospects for the preparation of new compounds designed in this way.

In order to elucidate the magnetic behavior of complexes of this type and to determine the effect of radical substituent on the ability to undergo VT and/or SCO mechanisms, here we performed quantum chemical calculations of the geometric, energy, and magnetic characteristics of cobalt pyridinophane complexes with *o*-benzoquinone containing 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (nitronyl nitroxide, NN) and (2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals (compounds **I** and **II**, respectively).



(I)



(II)

R = Me, Et, *i*-Pr, *t*-Bu

CALCULATION PROCEDURE

The calculations were carried out using the Gaussian 16 program [56] by the density functional theory (DFT) method using the UTPSSh functional [57, 58] and the 6-311++G(d,p) extended basis set. This combination adequately reproduces the energy and magnetic characteristics of complexes exhibiting magnetic bistability mechanisms [41–43, 59–65]. According to the results of calculations in this approximation for experimentally studied cobalt compounds, SCO takes place when $\Delta E_{HS-LS} < 6$ kcal/mol, while VT takes place when $\Delta E_{HS-LS} < 10$ kcal/mol [43]. Previously, it was shown that the outer-sphere counter-ions should be taken into account in the DFT studies of transition metal complexes with redox-active ligands [66]. Therefore, in the present study, we performed quantum chemical calculations for compounds containing the hexafluorophosphate anion. The stationary points on the potential energy surface (PES) were located by full optimization of the molecular structure geometry with stability check of the DFT wave function and calculation of the force constants. The exchange interaction parameters (J, cm^{-1}) were determined in terms of the broken symmetry (BS) formalism [67] using the generalized spin projection method proposed by Yamaguchi [68]. The graphical images of molecular structure were drawn using the ChemCraft program [69].

RESULTS AND DISCUSSION

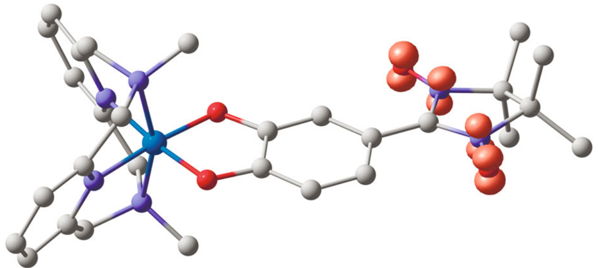
The ground state of complex **I** (R = Me) is the low-spin electronic isomer (electromer [70]) $_{LS}Co^{III}$Cat–NN containing a diamagnetic cobalt ion and diamagnetic catecholate form of the redox-ligand (Table 1). The only unpaired electron in this structure is localized on the radical NN moiety (Fig. 1). The $_{LS}Co^{II}$SQ–NN isomer found on the quartet PES is located 5.8 kcal/mol higher than the low-spin form. The significant destabilization (12.9 kcal/mol) of the $_{HS}Co^{II}$SQ–NN structure with high-spin cobalt ion attests that it is thermally unachievable. Thus, compound **I** (R = Me) would exist in a low-spin state over a wide temperature range, which is consistent with previous results for related compounds [31, 41–43] and indicates a minor effect of the nitronyl nitroxide radical on the energy characteristics of the complex. Meanwhile, the presence of the NN moiety in the molecule provides for the paramagnetism of the electromer $_{LS}Co^{III}$Cat–NN.

A study of complex **I** (R = Et) brought a similar result (Table 1): the significant destabilization of the high-spin structure $_{HS}Co^{II}$SQ–NN relative to the ground state $_{LS}Co^{III}$Cat–NN precludes rearrangements accompanied by a change in the spin state of the system.

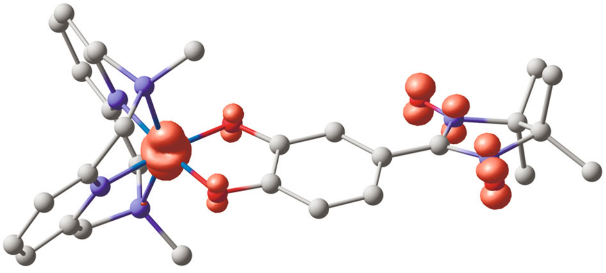
On going to compound **I** (R = *i*-Pr), the energy difference between the low-spin and high-spin isomers decreases to 9.7 kcal/mol (7.2 kcal/mol including ZPE); this implies the possibility of thermally initiated VT: $_{LS}Co^{III}$Cat–NN $\rightleftarrows$ $_{HS}Co^{II}$SQ–NN (Fig. 2). This behavior is in line with the theoretical and experimental data obtained for the 3,5-di-*tert*-butyl-*o*-benzoquinone cobalt complex with *N*-isopropyl-substituted pyridinophane [41]. Study of the exchange interactions in the electromer $_{HS}Co^{II}$SQ–NN shows a moderate antiferromagnetic coupling of unpaired electron spins of the metal ion with other radicals and strong ferromagnetic exchange between the SQ and NN moieties (Table 2), which allows one to expect that this structure would exist in the high-spin state over a wide temperature range. Thus, complex **I** (R = *i*-Pr) can undergo redox-isomeric transformations accompa-

Table 1. Spin (S), total energy without (E) and with inclusion of zero point vibrations (E^{ZPE}), the spin-squared operator (S^2), and relative energy without (ΔE) and with inclusion of zero point vibrations (ΔE^{ZPE}) for electromers of complexes **I** and **II** (R = Me, Et, *i*-Pr, *t*-Bu) calculated by DFT UTPSSh/6-311++G(d,p)

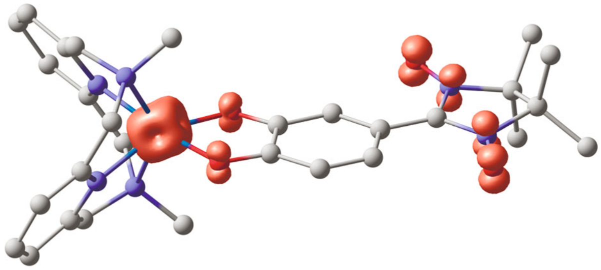
Electromer	S	E	E^{ZPE}	S^2	E	E^{ZPE}
		a.u.			kcal/mol	
I (R = Me)						
$_{LS}$Co^{III}Cat–NN	1/2	–4079.673906	–4079.041809	0.794	0.0	0.0
$_{LS}$Co^{II}SQ–NN	3/2	–4079.664656	–4079.034870	3.807	5.8	4.4
$_{HS}$Co^{II}SQ–NN	5/2	–4079.653341	–4079.025625	8.803	12.9	10.2
I (R = Et)						
$_{LS}$Co^{III}Cat–NN	1/2	–4158.327737	–4157.639282	0.794	0.0	0.0
$_{LS}$Co^{II}SQ–NN	3/2	–4158.319071	–4157.633135	3.807	5.4	3.9
$_{HS}$Co^{II}SQ–NN	5/2	–4158.306655	–4157.622437	8.802	13.2	10.6
I (R = *i*-Pr)						
$_{LS}$Co^{III}Cat–NN	1/2	–4236.977669	–4236.233267	0.794	0.0	0.0
$_{LS}$Co^{II}SQ–NN	3/2	–4236.972022	–4236.229827	3.807	3.5	2.2
$_{HS}$Co^{II}SQ–NN	5/2	–4236.962169	–4236.221770	8.802	9.7	7.2
I (R = *t*-Bu)						
$_{LS}$Co^{III}Cat–NN	1/2	–4315.607707	–4314.809305	0.795	2.8	3.8
$_{LS}$Co^{II}SQ–NN	3/2	–4315.612097	–4314.815432	3.807	0.0	0.0
$_{HS}$Co^{II}SQ–NN	5/2	–4315.600592	–4314.805657	8.802	7.2	6.1
II (R = Me)						
$_{LS}$Co^{III}Cat–TEMPO	1/2	–4028.961901	–4028.270447	0.754	0.0	0.0
$_{LS}$Co^{II}SQ–TEMPO	3/2	–4028.953434	–4028.264375	3.771	5.3	3.8
$_{HS}$Co^{II}SQ–TEMPO	5/2	–4028.941725	–4028.254331	8.766	12.7	10.1
II (R = Et)						
$_{LS}$Co^{III}Cat–TEMPO	1/2	–4107.615549	–4106.867821	0.754	0.0	0.0
$_{LS}$Co^{II}SQ–TEMPO	3/2	–4107.607851	–4106.862373	3.771	4.8	3.4
$_{HS}$Co^{II}SQ–TEMPO	5/2	–4107.595461	–4106.851488	8.766	12.6	10.2
II (R = *i*-Pr)						
$_{LS}$Co^{III}Cat–TEMPO	1/2	–4186.265312	–4185.461613	0.754	0.0	0.0
$_{LS}$Co^{II}SQ–TEMPO	3/2	–4186.260861	–4185.459493	3.771	2.8	1.3
$_{HS}$Co^{II}SQ–TEMPO	5/2	–4186.250585	–4185.451177	8.765	9.2	6.5
II (R = *t*-Bu)						
$_{LS}$Co^{III}Cat–TEMPO	1/2	–4264.895380	–4264.037976	0.754	3.4	4.2
$_{LS}$Co^{II}SQ–TEMPO	3/2	–4264.900850	–4264.044631	3.770	0.0	0.0
$_{HS}$Co^{II}SQ–TEMPO	5/2	–4264.889273	–4264.034735	8.766	7.3	6.2



$_{\text{LS}}$Co$^{\text{III}}$Cat–NN



$_{\text{LS}}$Co$^{\text{II}}$SQ–NN



$_{\text{HS}}$Co$^{\text{II}}$SQ–NN

Fig. 1. Spin density distribution (cutoff = 0.035 e/Å^3) in electromers of complex **I** (R = Me) according to the data of DFT UTPSSh/6-311++G(d,p) calculations. Here and in Figs. 2 and 3, the hydrogen atoms are omitted for clarity.

nied by a change in the spin state of the system (S) from 1/2 to 5/2.

The calculations for complex **I** (R = *t*-Bu) predict energy inversion of $_{\text{LS}}$Co$^{\text{III}}$Caτ–NN and $_{\text{LS}}$Co$^{\text{II}}$SQ–NN isomers, resulting in the latter being the ground state (Table 1). Destabilization of the electromer containing a low-spin trivalent cobalt ion is due to impossibility of formation of short (not exceeding 2.05 Å) Co–N bonds typical of this structure. This is caused by steric restrictions generated by bulky *tert*-butyl groups (Fig. 2). The high-spin $_{\text{HS}}$Co$^{\text{II}}$SQ–NN species is separated from the $_{\text{LS}}$Co$^{\text{II}}$SQ–NN ground state by 7.2 kcal/mol (6.1 kcal/mol including ZPE), which enables the $_{\text{LS}}$Co$^{\text{II}}$SQ–NN $\rightleftarrows$ $_{\text{HS}}$Co$^{\text{II}}$SQ–NN SCO process and is consistent with the data obtained previously for 3,5-di-*tert*-butyl-*o*-benzoquinone cobalt complex with *N*,*N*'-di-*tert*-butyl-2,11-diaza[3.3]-(2,6)pyridinophane [31, 41–43]. For the electromer $_{\text{HS}}$Co$^{\text{II}}$SQ–NN, like for the high-spin isomer of complex **I** (R = *i*-Pr) considered above, the calculations predicted moderate antiferromagnetic exchange interactions involving the metal ion and strong ferromagnetic coupling within the ligand (Table 2). Therefore, the variation of the alkyl groups at the nitrogen atoms of the tetraazamacrocycle does not change the nature and strength of exchange between the paramagnetic centers. The isomer $_{\text{LS}}$Co$^{\text{II}}$SQ–NN with a low-spin cobalt ion is characterized by the strong ferromagnetic coupling in the redox-active moiety (J_1 = 832 cm^{-1}), while the parameters J_2 and J_3 responsible for the Co$^{\text{II}}$–NN and SQ–NN exchange are close to the values found for $_{\text{HS}}$Co$^{\text{II}}$SQ–NN (Table 2).

It follows from the results given in Table 1 that the replacement of nitronyl nitroxide in *o*-benzoquinone ligand by TEMPO does not have a pronounced effect on the energy difference between the electromers of the complexes. The substantial destabilization of the high-spin isomers of coordination compounds **II** (R = Me, Et) indicates that the compounds under discussion exist in low-spin doublet state. The predicted energy gap between the electromers $_{\text{LS}}$Co$^{\text{III}}$Cat–TEMPO and $_{\text{HS}}$Co$^{\text{II}}$SQ-TEMPO of **II** (R = *i*-Pr) (Fig. 3) is 9.2 kcal/mol (6.5 kcal/mol including ZPE), which is indicative of the possibility of thermally initiated VT rearrangement. Compound **II** (R = *t*-Bu) containing *tert*-butyl groups at the nitrogen atoms of the pyridinophane ligand is expected to change its magnetic properties as a result of SCO (Table 1, Fig. 3).

Analysis of the J_1 values presented in Table 2 reveals strong ferromagnetic coupling in the $_{\text{LS}}$Co$^{\text{II}}$–SQ pair, whereas the high-spin isomer can exhibit a moderate antiferromagnetic exchange between the metal ion and semiquinone. TEMPO does not virtually interact with other paramagnetic centers (Table 2). It is noteworthy that the nature of exchange between the metal ion and SQ in compounds **I** and **II** (R = *i*-Pr, *t*-Bu) is similar to that found in electromers of the previously studied 3,5-di-*tert*-butyl-*o*-benzoquinone cobalt complexes [31, 41–43]. Therefore, the considered method of introduction of a radical into semiquinone does not modify the exchange interactions in the redox-active moiety. Meanwhile, the nature of the radical group (NN or TEMPO) determines the strength of the exchange coupling in which it participates.

Thus, the computer simulation of the geometric, energy, and magnetic characteristics of mononuclear cobalt complexes with *N*,*N*'-dialkyl-2,11-diaza[3.3]-(2,6)pyridinophanes and *o*-benzoquinone ligands containing nitronyl nitroxide or TEMPO demonstrated that the energy difference between isomers is determined by the bulkiness of alkyl substituent in the tetraazamacrocycle, but does not depend on the presence and type of the radical group. Compounds with

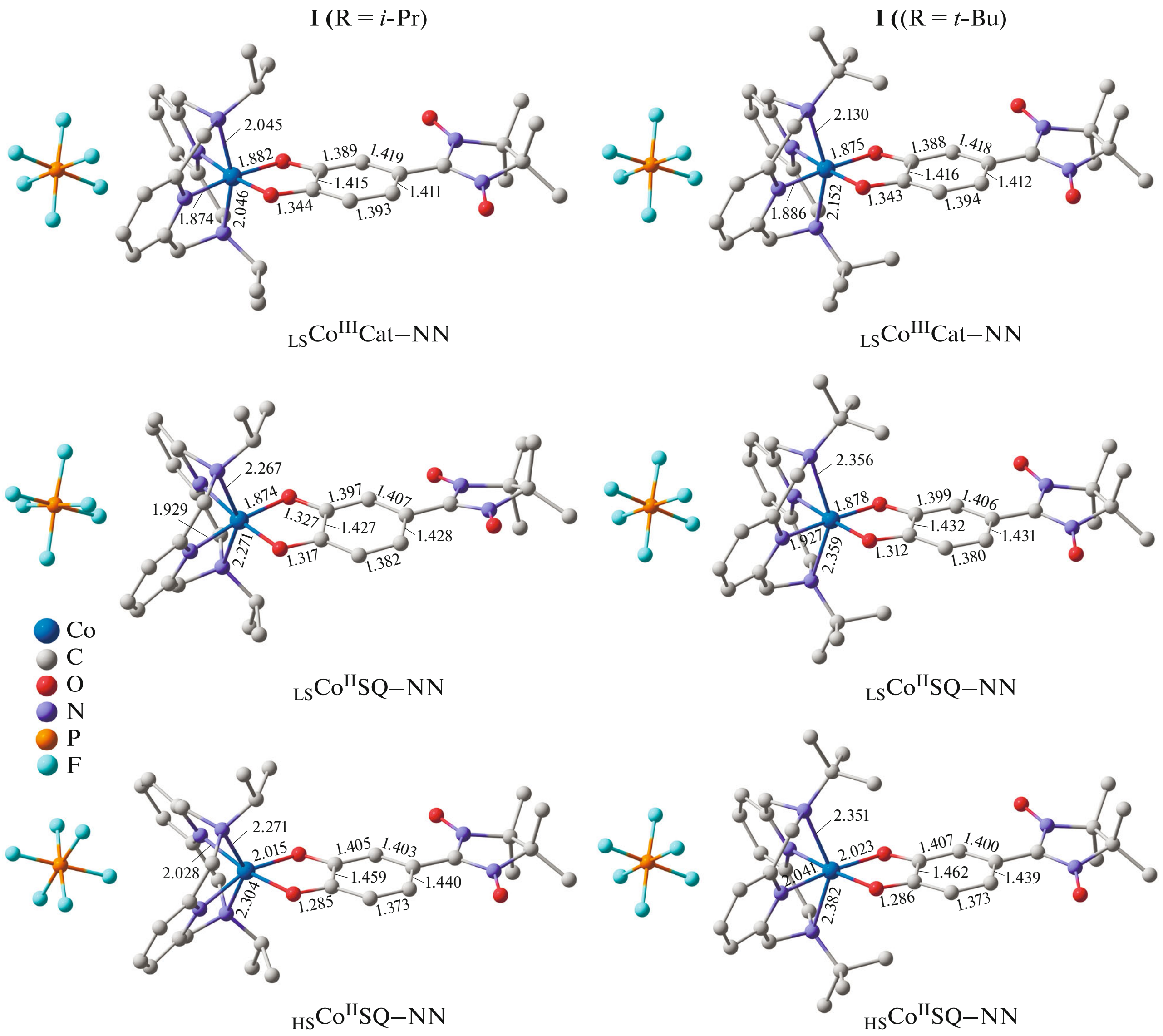


Fig. 2. Optimized geometries of electromers of complexes **I** (R = *i*-Pr, *t*-Bu) according to the data of DFT UTPSSh/6-311++G(d,p) calculations. Here an in Fig. 3, the bond lengths are in Angstroms.

Table 2. Spin (*S*) and exchange interaction parameter (*J*, cm^{-1}) for electromers ${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–NN}$, ${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–NN}$, ${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$, and ${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$ of complexes **I** and **II** (R = *i*-Pr, *t*-Bu) calculated by DFT UTPSSh/6-311++G(d,p)*

Electromer	S	J_1	J_2	J_3
		I (R = *i*-Pr)		
${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–NN}$	3/2	835	−71	529
${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–NN}$	5/2	−34	−59	898
		I (R = *t*-Bu)		
${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–NN}$	3/2	832	−47	438
${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–NN}$	5/2	−51	−14	610
		II (R = *i*-Pr)		
${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$	3/2	812	−3	4
${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$	5/2	−48	−2	3
		II (R = *t*-Bu)		
${}_{\text{LS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$	3/2	912	−5	5
${}_{\text{HS}}\text{Co}^{\text{II}}\text{SQ–TEMPO}$	5/2	−82	−5	2

* J_1 corresponds to the exchange between Co(II) and SQ, J_2 corresponds to the exchange between Co(II) and NN (TEMPO), and J_3 corresponds to the exchange between SQ and NN (TEMPO).

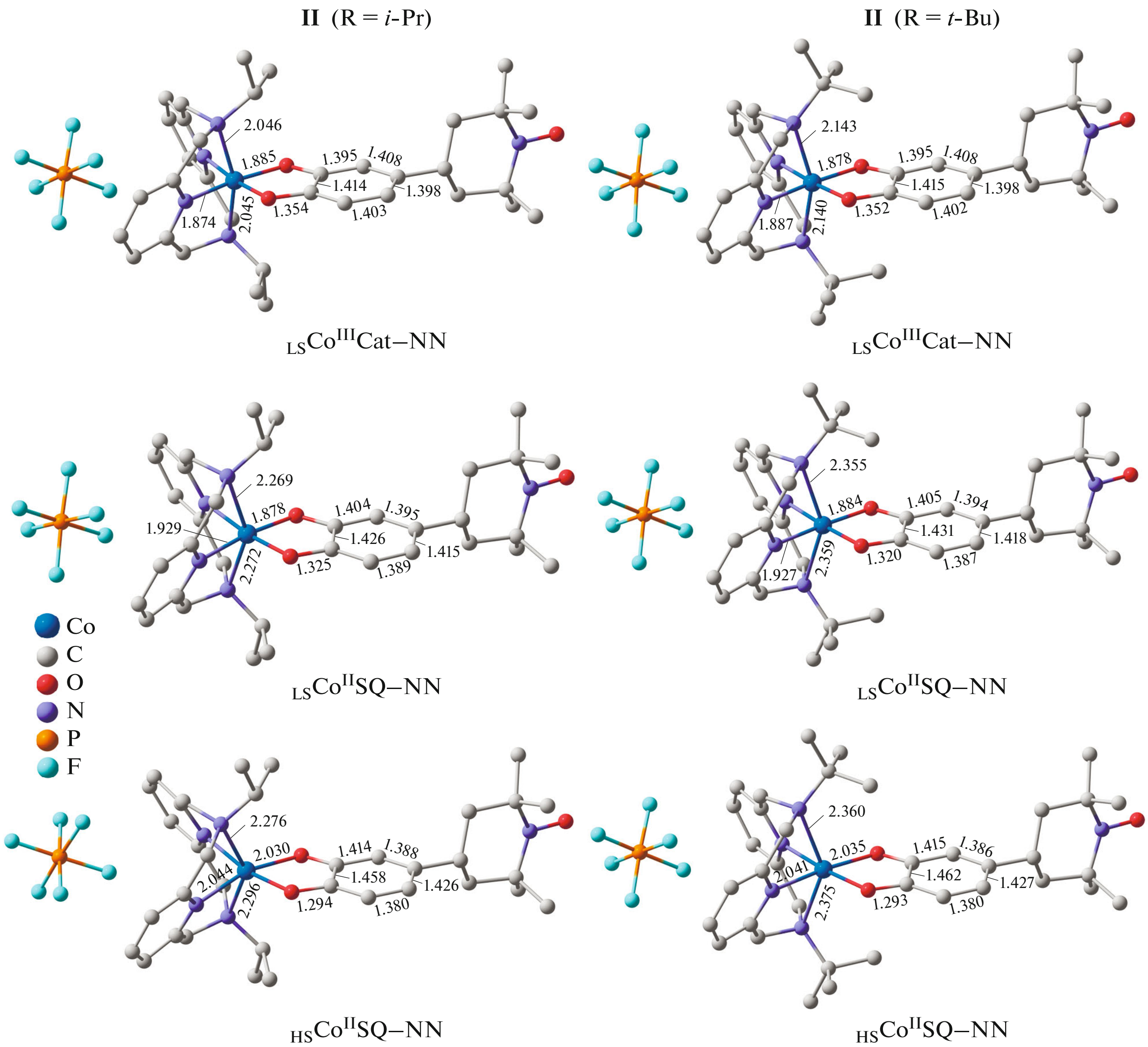


Fig. 3. Optimized geometries of electromers of complexes **II** (R = *i*-Pr, *t*-Bu) according to the data of DFT UTPSSh/6-311++G(d,p) calculations.

N-methyl- and *N*-ethyl-substituted pyridinophanes would occur in the low-spin state incorporating a trivalent metal ion. Complexes with *N*,*N*'-diisopropyl-2,11-diaza[3.3]-(2,6)pyridinophane are expected to undergo thermally initiated valence tautomeric rearrangement, while systems containing *tert*-butyl groups at the nitrogen atoms of the pyridinophane base are able to undergo spin crossover. An advantage of the studied compounds over existing analogues containing no radical substituents [19–31, 41–43] is the paramagnetism of all electromers, which expands the scope of potential applications of compounds of this type. A rational choice of the radical makes it possible to control the strength of exchange interactions in which it participates, with the exchange between the cobalt ion and semiquinone being invariable. The use of synthetically accessible structural motifs opens up the possibilities for the design of such complexes.

FUNDING

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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