ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 6, pp. 411–419. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 6, pp. 350–358.

Binuclear Di-*o*-Quinone Cobalt Complexes with the Acene Linker: Quantum Chemical Study of the Structures and Magnetic Properties

A. A. Starikova[a], *, **E. A. Metelitsa**[a], **and V. I. Minkin**[a]
[a] *Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*
**e-mail: alstar@ipoc.sfedu.ru*

Received November 12, 2018; revised January 17, 2019; accepted January 24, 2019

Abstract—The computer simulation (DFT UTPSSh/6-311++G(d,p)) of the structures and the energy and magnetic characteristics of the binuclear cobalt complexes bearing the tetraazamacrocyclic base and the di-*o*-quinone ligand containing as a linker the acene group is performed. Thus built molecules can undergo thermally switchable rearrangements of the spin states of the metal-centered moieties and photoinitiated single–triplet transitions of the acene linker. The possibility to control the magnetic properties of the studied coordination compounds using various external effects makes it possible to consider them as molecular switches.

Keywords: cobalt complexes, *o*-quinones, acenes, spin crossover, magnetic properties, quantum chemical simulation

DOI: 10.1134/S1070328419060095

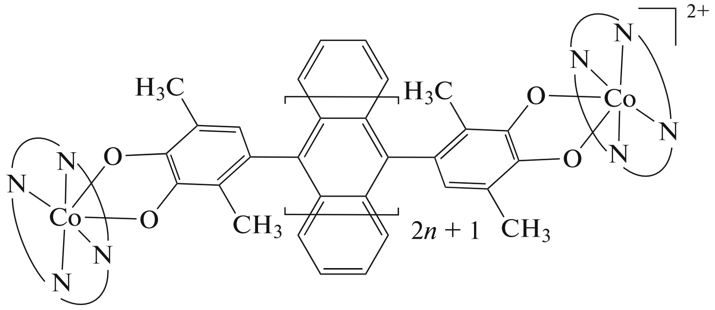
INTRODUCTION

Molecular design of transition metal complexes with the open shell demonstrating the variability of the magnetic properties depending on the applied external effect still remains an urgent challenge for specialists in the area of coordination chemistry. The possibility for the system to exist in two and more stable spin states caused by rearrangements via the mechanisms of spin crossover (SCO) [1] or valence tautomerism [2] is being studied in detail and reviewed comprehensively [3–6]. The magnetically active metal complexes can undergo reversible thermo- or photoinduced mutual transformations between electronic isomers (electromers [7]) with various chemical and physical properties, which makes them interesting objects for the development of displays, sensors, photosensitive materials, and spintronic devices [5, 8–10].

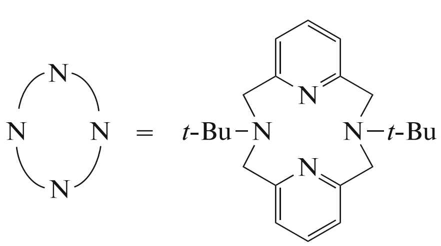
The cationic systems containing one redox-active ligand and a tetradentate macrocyclic nitrogen-containing base are among the well-studied types of coordination compounds that manifest effects of SCO and/or valence tautomerism [4, 11–14]. For example, the *o*-semiquinone (SQ) cobalt complex with *N*,*N*′-di-*tert*-butyl-2,11-diaza[3.3]-(2,6)pyridinophane can undergo the SCO effect rather rarely for compounds of this metal, which is determined by the transition ${}_{\mathrm{LS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ} \rightleftarrows {}_{\mathrm{HS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}$ instead of the expected valence tautomeric rearrangement [14]. According to the theoretical [15, 16] and experimental [14, 17] data, the discussed complex exhibits paramagnetism in the whole range of temperatures, because the diamagnetic state ${}_{\mathrm{LS}}\mathrm{Co}^{\mathrm{III}}\mathrm{Cat}$ including the trivalent cobalt ion and the catecholate (Cat) form of the redox-active ligand cannot be achieved.

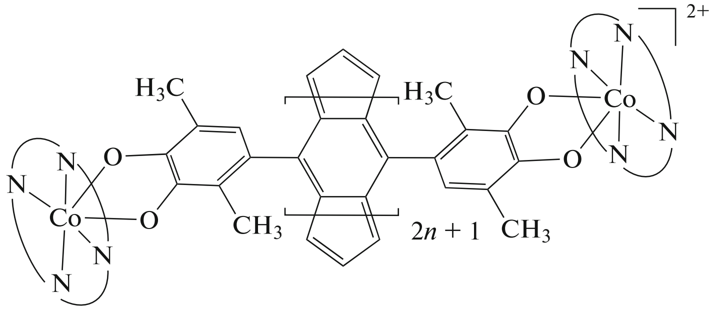
A series of the binuclear magnetically active compounds with the tetradentate di-*o*-quinone ligands was prepared on the basis of the above described structural motif [18–20]. Radical groups, for example, acenes (polycyclic hydrocarbons with linearly fused benzene rings), are used to impart an additional functionality to diamagnetic linkers of these complexes [21, 22]. These molecules are of special interest due to the dependence of their electronic structures on the length of the acene chain: the compounds containing more than six conjugated rings are stabilized as a singlet biradical that can be transformed into the triplet state by irradiation with the light of an appropriate wavelength [23–27]. The mutual influence of acene and *o*-benzoquinone groups was studied in the works [28, 29] devoted to the synthesis and investigation of the mononuclear cobalt complexes with the anthracene moiety.

We propose to join in one molecule two paramagnetic metal-containing centers potentially capable of undergoing rearrangements of the thermally initiated SCO and/or valence tautomerism and the acene linker group, whose singlet–triplet transitions are controlled by photoexcitation. The objects of this study are binuclear cobalt di-*o*-quinone complexes **I** and **II** in which the coordination sphere of the metal is completed by *N*,*N*′-di-*tert*-butyl-2,11-diaza[3.3]-(2,6)pyridinophane. The linker group in compounds **I** is presented by linear acene with various numbers of six-membered rings. The variation of the number of annelated cycles from three to seven (n = 0–2) makes it possible to study the influence of various spin states of the linker on the magnetic properties of the complex. A specific feature of compounds **II** is the presence of terminal five-membered rings in polycyclic hydrocarbon favoring, according to the experimental and theoretical data [30, 31], the stabilization of the triplet state already at five condensed cycles. The recent calculations [32] of the model systems with similar ligands showed that the character and strength of the exchange interactions between the paramagnetic centers depended on the structure of the polycyclic hydrocarbon chain. In the earlier studied binuclear di-*o*-quinone adducts of cobalt diketonates [33–35], the π-conjugated cyclic linker groups provided paramagnetism of all states of the complexes but they themselves remained diamagnetic. It is expected that in compounds **I** and **II** the biradical state of the acene moiety would result in an increase in the overall spin of the system and would favor the appearance of additional exchange channels.



I (n = 0–2)





II (n = 0–2)

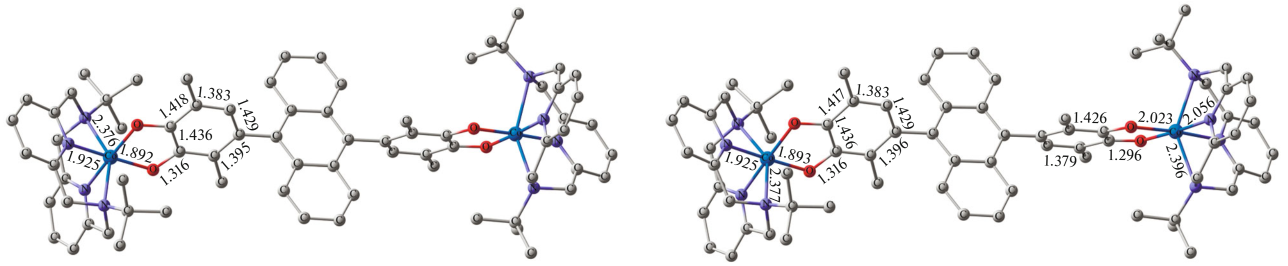
CALCULATION PROCEDURE

Calculations were performed using the Gaussian 09 program [36] by the density functional theory (DFT), UTPSSh functional [37, 38], and extended 6-311++G(d,p) basis set, the combination of which correctly reproduced the energy characteristics of the SCO in the cationic complexes [15, 16, 39–42]. The stationary points were localized on the potential energy surface 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 calculated in the framework of the broken symmetry (BS) formalism [43] using the generalized spin projection (GSP) method [44]. The graphical images of the molecular structures were obtained using the ChemCraft program [45].

RESULTS AND DISCUSSION

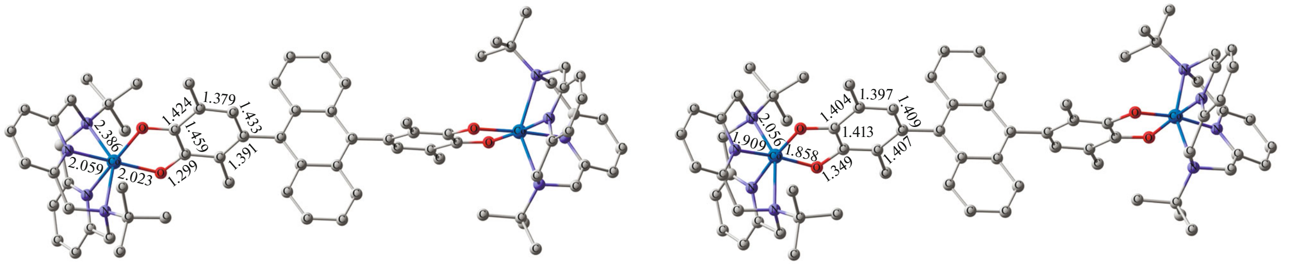
According to the calculation results, the most stable isomer of the dicationic cobalt di-*o*-quinone complex with the anthracene ligand **I** (n = 0) is the $_{\rm LS}\mathrm{Co^{II}SQ}$–$[\mathrm{C}]_n$–$[\mathrm{C}]_n$–$\mathrm{SQ}_{\rm LS}\mathrm{Co^{II}}$ structure on the quintet potential energy surface (S = 2) containing both metal ions in the low-spin divalent state and the biradical form (SQ–SQ) of the redox-active ligand (Fig. 1, Table 1). The discussed compound contains four paramagnetic centers due to the diamagnetism of the polycyclic –$[\mathrm{C}]_n$–$[\mathrm{C}]_n$– group. The exchange interactions in the metal-containing fragments $_{\rm LS}\mathrm{Co^{II}SQ}$ are strongly ferromagnetic (J = 535 cm^{-1}), whereas the lone electrons localized on semiquinones are antiferromagnetically coupled (J = –17 cm^{-1}) (Table 2).

The next in energy electromer $_{\rm LS}\mathrm{Co^{II}SQ}$–$[\mathrm{C}]_n$–$[\mathrm{C}]_n$–$\mathrm{SQ}_{\rm HS}\mathrm{Co^{II}}$ contains the divalent metal ions in



${}_{\mathrm{LS}}\mathrm{Co^{II}SQ{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}SQ_{LS}Co^{II}}$

${}_{\mathrm{LS}}\mathrm{Co^{II}SQ{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}SQ_{HS}Co^{II}}$



${}_{\mathrm{HS}}\mathrm{Co^{II}SQ{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}SQ_{HS}Co^{II}}$

${}_{\mathrm{LS}}\mathrm{Co^{III}Cat{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}Cat_{LS}Co^{III}}$

Fig. 1. Optimized geometries of the electromers of complex **I** ($n = 0$) calculated by the DFT UTPSSh/6-311++G(d,p) method. Here and in Fig. 2, hydrogen atoms are omitted for clarity, bond lengths are given in Å, and all structures have the charge +2.

different spin states. Its destabilization by 5.9 kcal/mol relative to the ground state makes it possible to expect SCO in one of the magnetically active moieties of the molecule with the transition of the system to the state with $S = 3$ (Table 1). The calculations predict moderate (Table 2) antiferromagnetic exchange interactions between spins of the lone electrons of the semiquinone and high-spin metal ion ($J = -92$ cm^{-1}). At the same time, a strong ferromagnetic coupling is retained in the opposite metal-containing center (${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}$).

The high-spin isomer ${}_{\mathrm{HS}}\mathrm{Co^{II}SQ{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}SQ_{HS}Co^{II}}$ is destabilized by 11.8 kcal/mol with respect to the ${}_{\mathrm{LS}}\mathrm{Co^{II}SQ{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}SQ_{LS}Co^{II}}$ electromer, which enables one to expect the second SCO rearrangement. This result is consistent with the studies of the mononuclear cobalt *o*-quinone complex with the di-*tert*-butyl derivative of pyridinophane, whose magnetic bistability is caused by the SCO transitions, and the character of exchange interactions in the metal-containing moieties (ferromagnetic in ${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}$ and antiferromagnetic in ${}_{\mathrm{HS}}\mathrm{Co^{II}SQ}$) is similar to that predicted for binuclear compound **I** ($n = 0$) [14–17].

The diamagnetic electromer ${}_{\mathrm{LS}}\mathrm{Co^{III}Cat{-}[C]_{\mathit{n}}{-}[C]_{\mathit{n}}{-}Cat_{LS}Co^{III}}$ containing the dicatecholate form of the redox-active ligand and low-spin trivalent cobalt ions is destabilized over the ground state by 18.0 kcal/mol (Table 1), which makes thermally initiated intramolecular redox processes improbable. Similar results were obtained for compounds **I** ($n = 1$) and **II** ($n = 0$).

It has previously been shown [30–32] that heptacene ($n = 2$) is a singlet biradical and the presence of terminal five-membered rings in polycyclic hydrocarbon favors the stabilization of the triplet state already at five fused cycles ($n = 1$). Compounds **I** ($n = 2$) and **II** ($n = 1$) were studied to reveal the influence of the biradical character of the acene moiety on the properties of the binuclear complexes.

The electromers of the discussion compounds are characterized by close geometric parameters (Fig. 2). The elongation of the polycyclic chain to the heptacene linker is not accompanied by substantial changes in the energy characteristics: the thermally initiated two-step SCO is expected in complex **I** ($n = 2$) (Table 1). The replacement of the terminal hexaatomic rings by five-membered cycles in the acene linker group does not result in the switching of the magnetic bistability mechanism of the metal center: according to the calculations, compound **II** ($n = 1$) can undergo two consecutive SCO transitions.

The electromers of complexes **I** ($n = 2$) and **II** ($n = 1$) with the biradical linkers contain six nonequivalent paramagnetic centers, which makes difficult the search for all (>50) spin states. Therefore, we studied model mononuclear compounds **III** ($n = 2$) and **IV** ($n = 1$) in which 16 (complex **III** ($n = 2$)) or 12 (compound **IV** ($n = 1$)) spin states (Fig. 3, Table 3) should be localized depending on the polycyclic chain structure and, correspondingly, on the spin density distribution.

Table 1. Spin (S), total energy (E), relative energy (ΔE), and operator of the squared spin (S^2) in the electromers of complexes **I** ($n = 0, 2$) and **II** ($n = 1$) calculated by the DFT UTPSSh/6-311++G(d,p) method

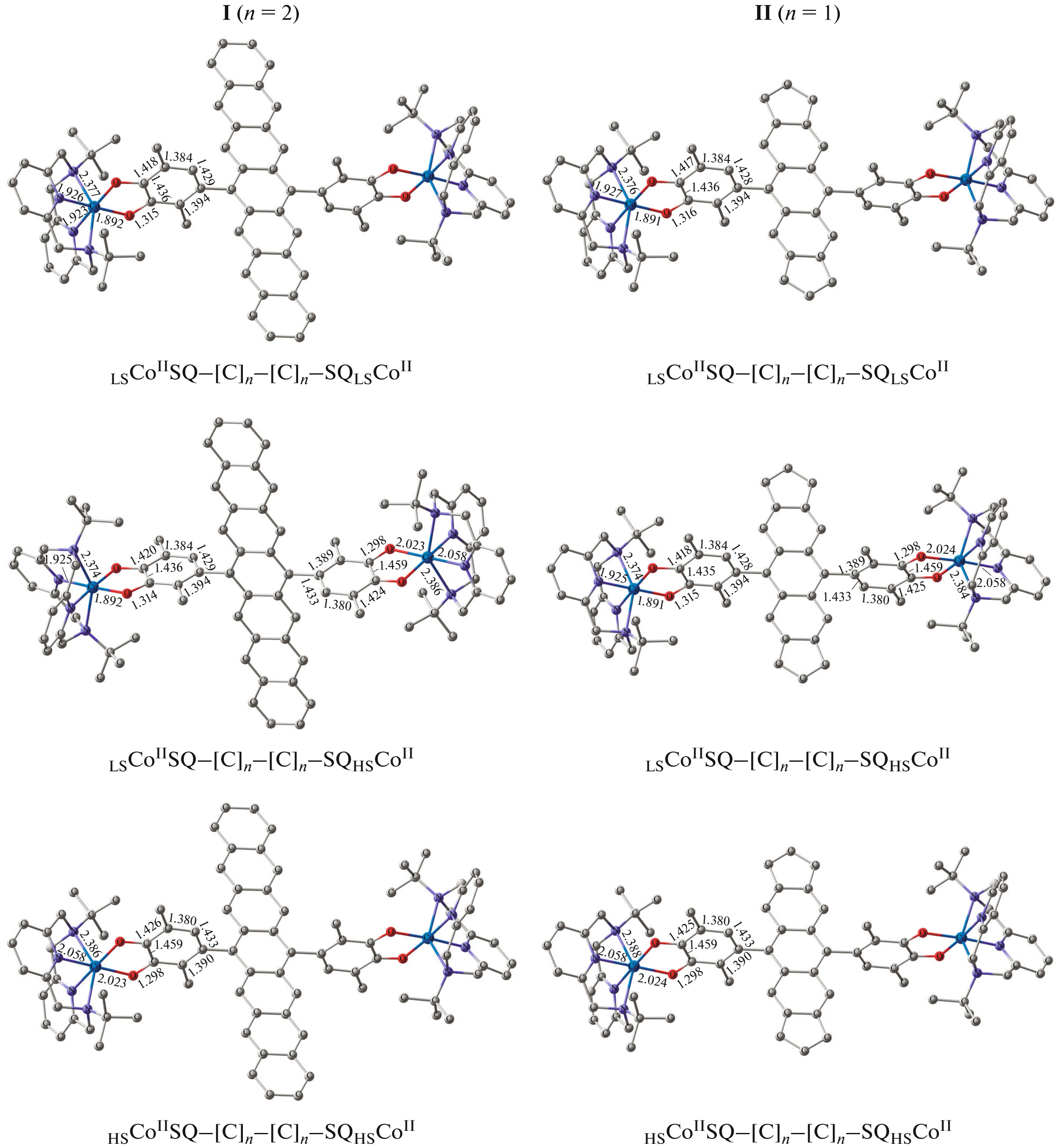
Electromer	S	E, au	ΔE, kcal/mol	S^2
I ($n = 0$)				
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{LS}Co^{II}$	2	–6377.080699	0.0	6.031
αββα*	0	–6377.075800		2.025
ααββ	0	–6377.080726		2.030
αβαβ	0	–6377.075847		2.023
αβαα = ααβα	1	–6377.078388		3.025
βααα = αααβ	1	–6377.078266		3.028
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	3	–6377.071280	5.9	12.027
αββα	1	–6377.069910		3.910
ααβα	2	–6377.072451		6.910
αβαα	2	–6377.068903		7.023
ααββ	1	–6377.071223		4.026
αααβ	0	–6377.072375		2.913
βααα	2	–6377.068112		7.026
βαβα	1	–6377.069996		3.908
${}_{HS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	4	–6377.061871	11.8	20.024
αββα	2	–6377.064069		7.794
ααββ	0	–6377.061918		4.023
αβαβ	0	–6377.064144		3.793
αβαα = ααβα	3	–6377.063425		12.909
βααα = αααβ	1	–6377.063003		4.909
${}_{LS}Co^{III}Cat–[C]_n–[C]_n–Cat_{LS}Co^{III}$	0	–6377.051979	18.0	0.000
I ($n = 2$)				
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{LS}Co^{II}$	3	–6991.796253	0.0	12.064
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	4	–6991.786625	6.0	20.060
${}_{HS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	5	–6991.777278	11.9	30.057
II ($n = 1$)				
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{LS}Co^{II}$	3	–6606.928851	0.0	12.082
${}_{LS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	4	–6606.919454	5.9	20.079
${}_{HS}Co^{II}SQ–[C]_n–[C]_n–SQ_{HS}Co^{II}$	5	–6606.909993	11.8	30.075

* The order of paramagnetic centers: 1, Co^{II}; 2, SQ; 3, SQ; and 4, Co^{II}; α corresponds to the up orientation of spins, and β corresponds to the down orientation of spins.

Table 2. Parameters of exchange interactions between the paramagnetic centers (J*, cm^{-1}) in the electromers of complex **I** ($n = 0$) calculated by the DFT UTPSSh/6-311++G(d,p) method

Electromer	J_{1-2}	J_{1-3}	J_{1-4}	J_{2-3}	J_{2-4}	J_{3-4}
${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{LS}Co^{II}$	535	1	9	−17	1	535
${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$	570	47	15	−49	−10	−92
${}_{HS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$	−78	1	4	−53	1	−78

* The order of paramagnetic centers: 1, Co^{II}; 2, SQ; 3, SQ; and 4, Co^{II}.

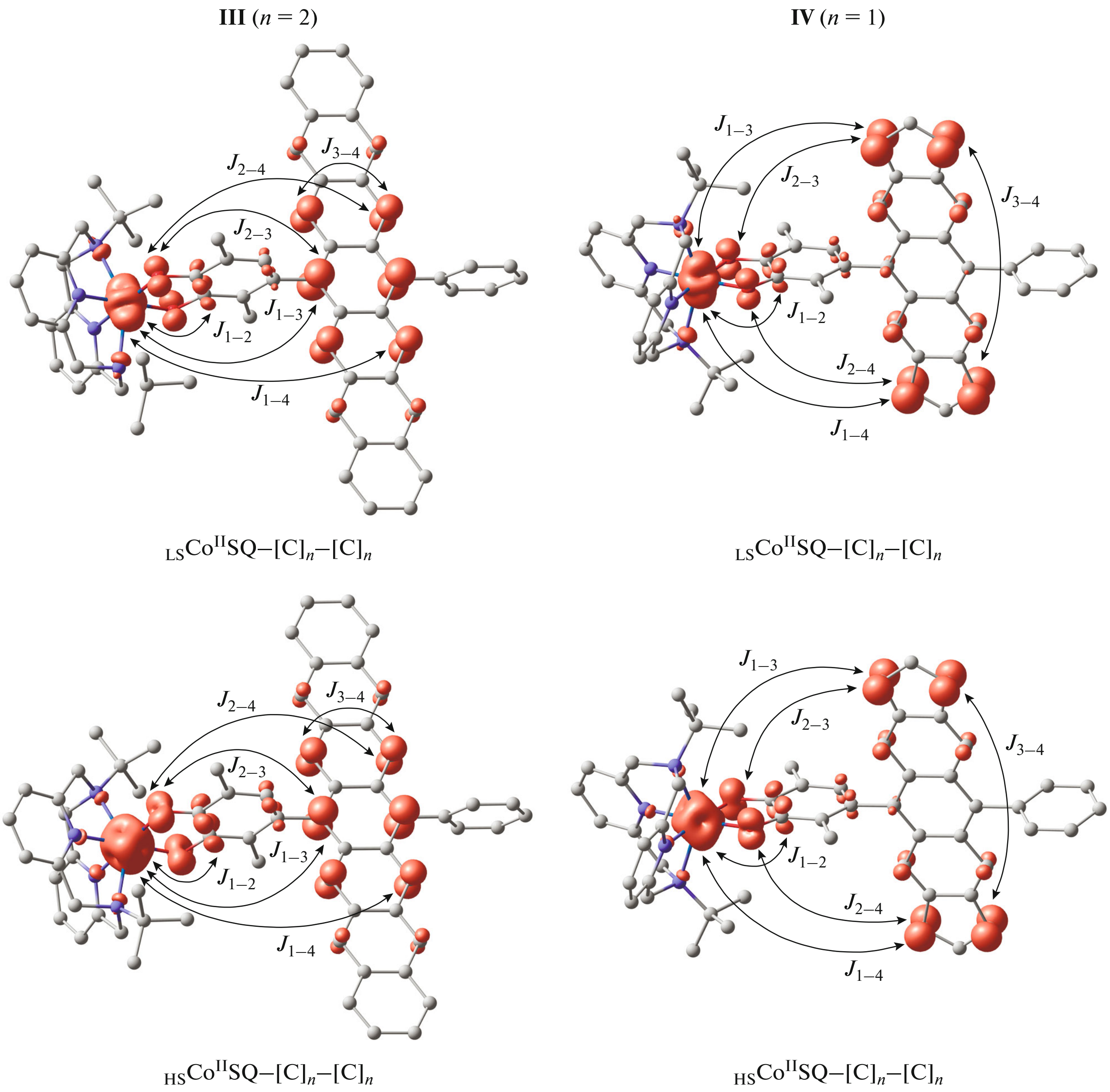


${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{LS}Co^{II}$ ${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{LS}Co^{II}$

${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$ ${}_{LS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$

${}_{HS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$ ${}_{HS}Co^{II}SQ-[C]_n-[C]_n-SQ_{HS}Co^{II}$

Fig. 2. Optimized geometries of the electromers of complexes **I** ($n = 2$) and **II** ($n = 1$) calculated by the DFT UTPSSh/6-311++G(d,p) method.



III ($n = 2$) **IV** ($n = 1$)

$_{\mathrm{LS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}–[\mathrm{C}]_n–[\mathrm{C}]_n$ $_{\mathrm{LS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}–[\mathrm{C}]_n–[\mathrm{C}]_n$

$_{\mathrm{HS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}–[\mathrm{C}]_n–[\mathrm{C}]_n$ $_{\mathrm{HS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}–[\mathrm{C}]_n–[\mathrm{C}]_n$

Fig. 3. Spin density distribution and the scheme of exchange interactions in the electromers of monocationic complexes **III** ($n = 2$) and **IV** ($n = 1$) calculated by the DFT UTPSSh/6-311++G(d,p) method. Hydrogen atoms are omitted; cutoff = 0.012.

The calculations show (Table 4) that, regardless of the type of terminal rings, the acene linker is stabilized as a singlet biradical demonstrating a strong antiferromagnetic coupling ($J < -1200$ cm^{-1}). As follows from the results of previous calculations [32], the energy band gap between the singlet (biradical) and triplet forms does not exceed 7 kcal/mol, which will facilitate the transition of acene to the high-spin state under light irradiation. The spin density in heptacene is concentrated in the central moiety of the linker on the opposite carbon atoms of the polyaromatic chain (Fig. 3). Another spin density distribution was found in complex **IV** ($n = 1$): the paramagnetic centers of the polycyclic fragment of this compound are located on the carbon atoms of the terminal five-membered cycles. The exchange interactions of the lone electrons of semiquinones and metal ions are of the same character as those in the above considered compounds with the diamagnetic linker (Tables 2, 4). A strong ferromagnetic coupling ($J > 400$ cm^{-1}) was predicted for the low-spin $_{\mathrm{LS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}$ fragment, and the spins of the lone electrons in the $_{\mathrm{HS}}\mathrm{Co}^{\mathrm{II}}\mathrm{SQ}$ pair interact antiferromagnetically (from -150 to -180 cm^{-1}). Based on the obtained data, we may conclude that the length and

Table 3. Spin (S), total energy (E), relative energy (ΔE), and operator of the squared spin (S^2) in the electromers of complexes **III** ($n = 2$) and **IV** ($n = 1$) calculated by the DFT UTPSSh /6-311++G(d,p) method

Electromer	S	E_{tot}, au	ΔE, kcal/mol	S^2
III ($n = 2$)				
${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	2	−4304.242415	0.0	6.049
βααα	1	−4304.240163		3.046
αβαα	1	−4304.245173		2.620
ααβα	1	−4304.258210		2.339
αααβ	1	−4304.251347		2.804
αββα	0	−4304.250469		1.212
αβαβ	0	−4304.251247		1.215
ααββ	0	−4304.243191		1.080
${}_{\mathrm{HS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	3	−4304.232424	6.3	12.045
βααα	0	−4304.234113		2.924
αβαα	2	−4304.238073		6.517
ααβα	2	−4304.250196		6.122
αααβ	2	−4304.244502		6.115
αββα	1	−4304.252272		3.152
αβαβ	1	−4304.252269		3.215
ααββ	1	−4304.239408		3.732
IV ($n = 1$)				
${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	2	−3919.375659	0.0	6.067
βααα	1	−3919.373404		3.064
αβαα	1	−3919.376365		2.795
ααβα = αααβ	1	−3919.385819		2.500
αββα = αβαβ	0	−3919.383777		1.483
ααββ	0	−3919.380934		1.681
${}_{\mathrm{HS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	3	−3919.365839	6.2	12.064
βααα	0	−3919.367287		2.941
αβαα	2	−3919.374075		6.538
ααβα = αααβ	2	−3919.375752		6.519
αββα = αβαβ	1	−3919.378008		3.368
ααββ	1	−3919.371366		3.496

* The order of paramagnetic centers: 1, Co$^{\mathrm{II}}$; 2, SQ; 3, $[\mathrm{C}]_n$; and 4, $[\mathrm{C}]_n$; α corresponds to the up orientation of spins, and β corresponds to the down orientation.

Table 4. Parameters of exchange interactions between the paramagnetic centers (J*, cm^{-1}) in the electromers of complexes **III** ($n = 2$) and **IV** ($n = 1$) calculated by the DFT UTPSSh/6-311++G(d,p) method

Electromer	J_{1-2}	J_{1-3}	J_{1-4}	J_{2-3}	J_{2-4}	J_{3-4}
III ($n = 2$)						
${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	426	−81	556	−503	82	−1694
${}_{\mathrm{HS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	−183	−160	49	−785	−241	−1832
IV ($n = 1$)						
${}_{\mathrm{LS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	610	−123	−123	−388	−388	−1277
${}_{\mathrm{HS}}\mathrm{Co^{II}SQ}{-}[\mathrm{C}]_n{-}[\mathrm{C}]_n$	−154	23	23	−544	−544	−1207

* The order of paramagnetic centers: 1, Co$^{\mathrm{II}}$; 2, SQ; 3, $[\mathrm{C}]_n$; and 4, $[\mathrm{C}]_n$.

structure of the acene fragment of binuclear complexes **I** and **II** exert no substantial effect on the possibility of manifesting rearrangements accompanied by the switch of the spin states. At the same time, the biradical linker favors the appearance of the additional exchange channels $_{\rm LS}$Co$^{\rm II}$–[C]$_n$, $_{\rm HS}$Co$^{\rm II}$–[C]$_n$, and SQ–[C]$_n$ (Table 4), whose characteristics can be controlled by the variation of the turning angle of the quinone ring relative to the polycyclic chain [46].

To conclude, it was shown by the quantum chemical calculations (DFT UTPSSh/6-311++G(d,p)) that the complex formation of the tetradentate di-*o*-quinone ligands bearing the acene linker groups with the cobalt compounds can afford the systems manifesting thermally switchable spin states of the metal-centered fragments and photocontrolled singlet–triplet transitions of the polycyclic linker. The mechanism of magnetic bistability of these complexes is determined by the nature of the tetraazamacrocyclic ligands, whereas the magnetic behavior of the complex depends on the structure of the acene chain. The spin states of compounds **I** ($n > 1$) and **II** ($n > 0$) varied in a wide range allow one to consider these compounds as efficient molecular switches with the magnetic response function.

The proposed approach to the design of binuclear molecules with the ligands containing redox-active and photoexcited moieties makes it possible to form a basis for the structural design of the polyspin coordination compounds, whose magnetic properties are controlled by independent external sources. The choice of the objects of the present study is based on an analysis of the existing procedures for the preparation of similar mononuclear *o*-quinone complexes with the acene fragments [28, 29] and the binuclear cobalt compounds with the tetraazamacrocyclic ligands [18–20], which enables one to expect that the systems studied in this work would be synthesized.

FUNDING

This work was supported by the Council for Grants of the President of the Russian Federation, grant no. MK-1386.2018.3.

REFERENCES

1. *Spin-Crossover in Transition Metal Compounds I: Topics in Current Chemistry*, Gutlich, P. and Goodwin, H.A., Eds., Berlin–Springer, 2004, vol. 233.
2. Buchanan, R.M. and Pierpont, C.G., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 4951.
3. *Spin-Crossover Materials: Properties and Applications*, Halcrow, M.A., Ed., Chichester: Wiley, 2013.
4. Tezgerevska, T., Alley, K.G., and Boskovic, C., *Coord. Chem. Rev.*, 2014, vol. 268, p. 23.
5. Sato, O., *Nat. Chem.*, 2016, vol. 8, no. 7, p. 644.
6. Starikova, A.A. and Minkin, V.I., *Russ. Chem. Rev.*, 2018, vol. 87, no. 11, p. 1049.
7. Bally, T., *Nat. Chem.*, 2010, vol. 2, no. 3, p. 165.
8. Calzolari, A., Chen, Y., Lewis, G.F., et al., *J. Phys. Chem. B*, 2012, vol. 116, no. 43, p. 13141.
9. Ferrando-Soria, J., Vallejo, J., Castellano, M., et al., *Coord. Chem. Rev.*, 2017, vol. 339, p. 17.
10. Senthil Kumar, K. and Ruben, M., *Coord. Chem. Rev.*, 2017, vol. 346, p. 176.
11. Bencinia, A., Caneschia, A., Carbonera, C., et al., *J. Mol. Struct.*, 2003, vol. 656, nos. 1–3, p. 141.
12. Beni, A., Dei, A., Laschi, S., et al., *Chem.-Eur. J.*, 2008, vol. 14, no. 6, p. 1804.
13. Kruger, H.-J., *Coord. Chem. Rev.*, 2009, vol. 253, nos. 19–20, p. 2450.
14. Graf, M., Wolmershauser, G., Kelm, H., et al., *Angew. Chem., Int. Ed. Engl.*, 2010, vol. 49, no. 5, p. 950.
15. Starikov, A.G., Starikova, A.A., and Minkin, V.I., *Dokl. Chem.*, 2016, vol. 467, no. 1, p. 83.
16. Starikova, A.A., Chegerev, M.G., Starikov, A.G., and Minkin, V.I., *Comp. Theor. Chem.*, 2018, vol. 1124, p. 15.
17. Rupp, F., Chevalier, K., Graf, M., et al., *Chem.-Eur. J.*, 2017, vol. 23, no. 9, p. 2119.
18. Min, K.S., DiPasquale, A.G., Rheingold, A.L., et al., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 17, p. 6229.
19. Teki, Y., Shirokoshi, M., Kanegawa, S., and Sato, O., *Eur. J. Inorg. Chem.*, 2011, p. 3761.
20. Madadi, A., Itazaki, M. Gable, R.W., et al., *Eur. J. Inorg. Chem.,* 2015, p. 4991.
21. Anthony, J.E., *Chem. Rev.*, 2006, vol. 106, no. 12, p. 5028.
22. Bettinger, H.F., *Pure Appl. Chem.*, 2010, vol. 82, no. 4, p. 905.
23. Anthony, J.E., *Angew. Chem., Int. Ed. Engl.*, 2008, vol. 47, no. 3, p. 452.
24. Mondal, R., Tönshoff, C., Khon, D., et al., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 40, p. 14281.
25. Zade, S.S. and Bendikov, M., *Angew. Chem., Int. Ed. Engl.*, 2010, vol. 49, no. 24, p. 4012.
26. Zuzak, R., Dorel, R., Kolmer, M., et al., *Angew. Chem., Int. Ed. Engl.*, 2018, vol. 57, no. 33, p. 10500.
27. Shen, B., Tatchen, J., Sanchez-Garcia, E., and Bettinger, H.F., *Angew. Chem., Int. Ed. Engl.*, 2018, vol. 57, no. 33, p. 10506.
28. Katayama, K., Hirotsu, M., Kinoshitaand, I., and Teki, Y., *Dalton Trans.*, 2014, vol. 43, no. 35, p. 13384.
29. Katayama, K., Hirotsu, M., Ito, A., and Teki, Y., *Dalton Trans.*, 2016, vol. 45, no. 25, p. 10165.
30. Rudebusch, G.E., Zafra, J.L., Jorner, K., et al., *Nat. Chem.*, 2016, vol. 8, no. 8, p. 753.
31. Nakano, M., Fukuda, K., and Champagne, B., *J. Phys. Chem. C*, 2016, vol. 120, no. 2, p. 1193.
32. Starikova, A.A. and Minkin, V.I., *Comp. Theor. Chem.*, 2018, vol. 1138, p. 163.
33. Minkin, V.I., Starikov, A.G., and Starikova, A.A., *Dalton Trans.*, 2015, vol. 44, no. 40, p. 17819.
34. Starikova, A.A., Starikov, A.G., and Minkin, V.I., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 4, p. 197. https://doi.org/10.1134/S1070328417040066

35. Minkin, V.I., Starikova, A.A., and Starikov, A.G., *Russ. Chem. Bull.*, 2017, vol. 66, no. 9, p. 1543. doi 10.1134/S1070328417040066

36. Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., *Gaussian-09. Revision E. 01*, Wallingford: Gaussian, 2013.

37. Tao, J.M., Perdew, J.P., Staroverov, V.N., and Scuseria, G.E., *Phys. Rev. Lett.*, 2003, vol. 91, no. 14, p. 146401.

38. Staroverov, V.N., Scuseria, G.E., Tao, J., and Perdew, J.P., *J. Chem. Phys.*, 2003, vol. 119, no. 23, p. 12129.

39. Bannwarth, A., Schmidt, S.O., Peters, G., et al., *Eur. J. Inorg. Chem.*, 2012, no. 16, p. 2776.

40. Cirera, J. and Paesani, F., *Inorg. Chem.*, 2012, vol. 51, no. 15, p. 8194.

41. Starikova, A.A. and Minkin, V.I., *Russ. J. Coord. Chem.*, 2018, vol. 44, no. 8, p. 483. https://doi.org/10.1134/S1070328418080079

42. Starikov, A.G., Starikova, A.A., Chegerev, M.G., and Minkin, V.I., *Russ. J. Coord. Chem.*, 2019, vol. 45, no. 2, p. 105. https://doi.org/10.1134/S1070328419020088

43. Noodleman, L., *J. Chem. Phys.*, 1981, vol. 74, no. 10, p. 5737.

44. Shoji, M., Koizumi, K., Kitagawa, Y., et al., *Chem. Phys. Lett.*, 2006, vol. 432, nos. 1–3, p. 343.

45. Chemcraft. Version 1.7. 2013: http://www.chemcraft-prog.com

46. Minkin, V.I., Starikov, A.G., Starikova, A.A., et al., *Dalton Trans.*, 2018, vol. 47, no. 44, p. 15948.

Translated by E. Yablonskaya