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Adducts of cobalt(II) bis(salicylaldiminates) and redox-active phenoxazin-1-one: synthesis, structure, and magnetic properties

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Adducts of cobalt(II) bis(salicylaldiminates) and 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one were synthesized and their molecular and crystal structures were determined. According to the ESR and magnetochemical data, the metal atom is in the low-spin trivalent state (Co^{III}) due to the intramolecular electron transfer to the redox-active ligand. In the solid state, the mixed-ligand complexes are stable in air for several months, but in solution at elevated temperatures they dissociate to the starting components. Such a behavior detected by the temperature dependence of the effective magnetic moment is explained by the quantum chemical DFT calculations of the energy barriers of possible valence tautomeric dynamics, whose values were found to be higher than the enthalpy of dissociation.

Key words: complexes, phenoxazin-1-one, magnetic properties, valence tautomerism.

Considerable interest in studying the structures and magnetoswitchable properties of bistable transition metal complexes with redox-active (non-innocent) ligands is caused by the possibility to produce from them molecular switches,[1—3] molecular memory devices,[4—6] displays,[7—9] and holographic devices.[10,11] The mechanism of thermo- or photocontrolled rearrangements of these complexes (redox isomerism or valence tautomerism) is determined by the intramolecular electron transfer between the metal ion and ligand system. This effect most frequently appears in the complexes of hexacoordinate cobalt and manganese with two sterically hindered *o*-quinones or their imino derivatives in which the coordination saturation of the central ion is provided by the addition of a neutral bidentate ligand with donor nitrogen atoms.[12,13]

The other approach to the synthesis of metal complexes capable of exhibiting valence tautomerism is the formation of a stable complex of the tetracoordinate metal with the bidentate redox-active ligand. The intramolecular redox processes expected in these associates will be caused by the transition of the redox-active ligand from the neutral (BQ) to radical-anion (SQ) form. One of the first reports devoted to the study of complexes of this type was published in 1973.[14] The authors considered the interaction of the Co^{II} and Fe^{II} salicylalethylenediaminate complexes with *p*- and *o*-benzoquinones, 9,10-phenanthrenequinone, and 1,2-naphthoquinone. The adducts of other planar Co^{II} complexes with *o*-benzoquinone were studied further. These studies showed that the reaction was accompanied by the metal-to-ligand electron transfer in all cases.[15—18] The adduct formation of Co^{II} acetylacetonate with *o*-benzoquinone was studied by Kabachnik and coauthors.[19] In all above works, metal oxidation to the trivalent state and ligand transition to the *o*-semiquinone form were observed.

The mixed-ligand complexes of bis(acetylacetonato)ruthenium with *o*-imino-, *o*-iminothioquinones, and *o*-diiminoquinones **1** were described and structurally characterized.[20,21]

The structure formed due to the electron transfer from the Ru^{2+} ion to the lowest unoccupied π*-MO of iminoquinone was ascribed to complex **1** (X = O) (Scheme 1) on the basis of the values of C—O and C—N bond lengths typical of the iminosemiquinone form of the redox-active ligand and spectroelectrochemical data. At the same time, valence tautomerism was reported for none of the synthesized adducts.

In this work, we showed the possibility of synthesizing wide series of mixed-ligand hexacoordinate cobalt com-

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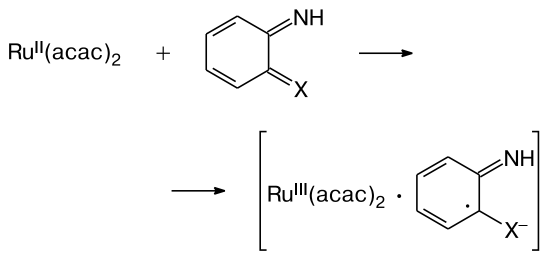
Scheme 1



1

X = O, S

plexes **2** formed by the interaction of redox-active 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (**3**) with tetrahedral cobalt(II) bis(salicylaldiminates) **4**. Complexes **2** stable in air are formed due to two consecutive reactions: coordination of the redox-active ligand and intramolecular one-electron oxidation by this ligand of the tetrahedral high-spin $\mathrm{Co^{II}}$ complex to form the octahedral low-spin $\mathrm{Co^{III}}$ complex (Scheme 2).

The molecular structures of complexes **2a** and **2b** were determined[22] by X-ray diffraction analysis (Fig. 1).

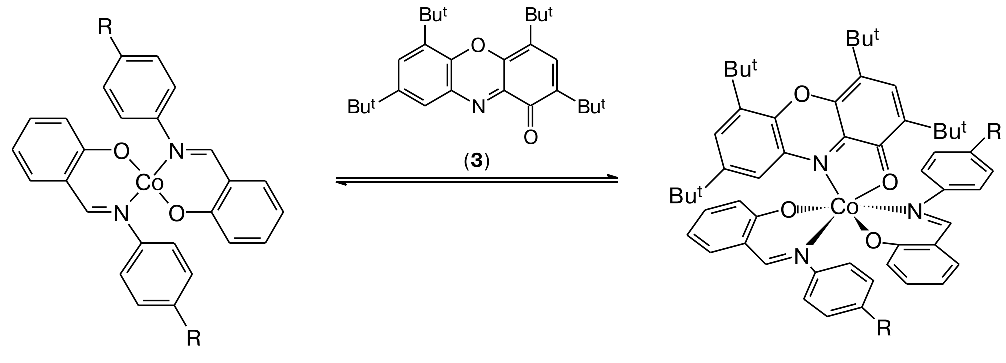
Both molecular and crystal structures of complexes **2a** and **2b** are virtually identical (Table 1). Insignificant differences are caused by different amounts of solvate acetonitrile molecules, namely, 1.4 and 1 in **2a** and **2b**, respectively. In turn, the variation of the number of solvate molecules results in different numbers of symmetrically independent molecules of the complex (one in **2a** and two in **2b**) and, as a consequence, in doubling parameter *c* in complex **2b**. The central cobalt atom is characterized by a slightly distorted octahedral configuration. The five-membered metallocycles Co(1)O(2)C(2)C(1)N(1) in complexes **2a** and **2b** adopt the *envelope* conformations with the cobalt atom shifted from the plane, whereas the conformation of the six-membered rings for two ligands differs for each complex. The Co(1)N(2)C(35)C(30)C(29)O(3) cycle has a *chair* conformation with the deviation of the cobalt atom, whereas the O(4) atom shifts from the plane in the Co(1)N(3)C(49)C(44)C(43)O(4) cycle. The observed conformational differences do not result in a significant variation of the bond lengths with both metal atom and in six-membered metallocycles and are probably caused by shortened intramolecular contacts in crystals **2a** and **2b**. Indeed, in the case of the metallocycles with the deviation of the oxygen atom, the aryl substituent at the N(3) atom lies above the plane of the redox ligand and forms shortened contacts C(55)...C(1) and C(50)...N(1), which do not differ virtually for both structures and lie in the ranges 3.077(4)—3.193(4) and 2.849(4)—2.877(4) Å. Although the formation of these shortened contacts has, very probably, a forced character (for steric reasons), it cannot be excluded that similar stacking interactions can act as a possible channel of charge transfer.

The C(2)—O(2) (1.312(3)—1.315(4) Å), N(1)—C(1) (1.366(4)—1.375(4) Å), and C(1)—C(2) (1.417(5)—1.429(4) Å) bond lengths in the five-membered cycle formed by the central cobalt atom with the donor centers of the redox ligand are consistent with the mean values of these bond lengths for the ligands in the iminosemiquinone (ISQ) form in the complexes of the Third Period metals.[23] It should be mentioned that the matrix of root-mean-square amplitudes of shifts of the cobalt atom is fairly isotropic in both structures, which also indirectly indicates the absence of a superposition of different spin states of the metal atom.[24]

Thus, the data obtained indicate the stabilization of the radical-anion (ISQ) structure of the redox-active ligand in complexes **2** formed due to the intramolecular electron transfer from the $\mathrm{Co^{2+}}$ ion (Scheme 3).

The radical-ion form of the redox-active ligand (ISQ) in complexes **2a** and **2b** is confirmed by the data of ESR spectroscopy. The spectrum of the crystalline sample of complex **2b** is a singlet with $\Delta H = 120$ G and $g = 1.9948$.

Scheme 2



4a,b

2a,b

R = H (**a**), Me (**b**)

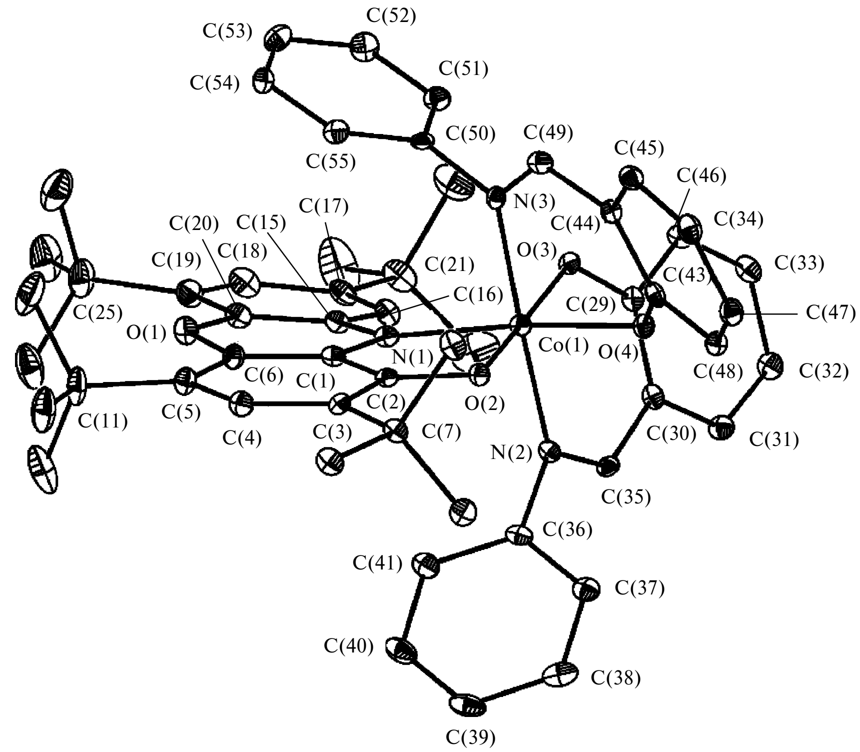


Fig. 1. Molecular structure of complex ISQ-**2a**. The numeration of atoms in complex **2b** is identical. The solvent molecules and hydrogen atoms are omitted.

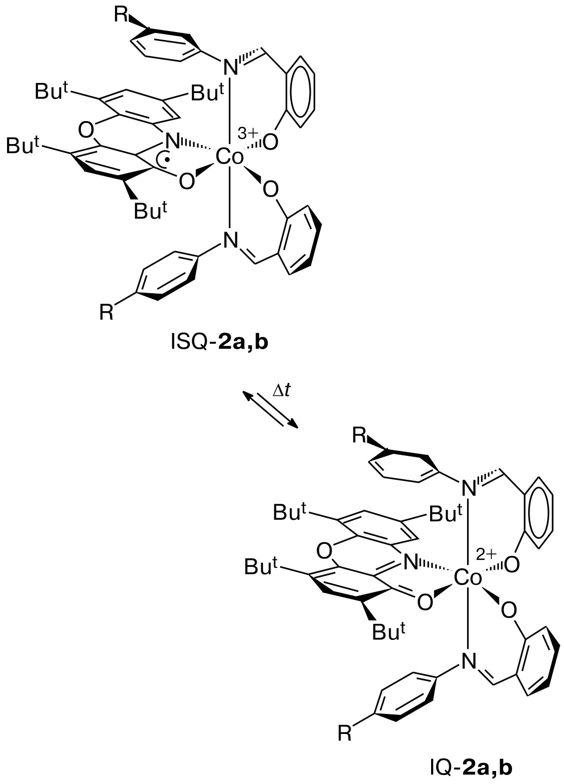
Table 1. Bond lengths (*d*) and bond angles (ω) in **2a** and in one of the independent ISQ-**2b** molecules

Bond	*d*/Å	
	2a	**2b**
Co(1)—O(2)	1.873(2)	1.885(2)
Co(1)—O(3)	1.893(2)	1.885(2)
Co(1)—O(4)	1.886(2)	1.886(2)
Co(1)—N(1)	1.975(3)	1.976(3)
Co(1)—N(2)	1.952(3)	1.957(3)
Co(1)—N(3)	1.958(3)	1.950(3)
O(1A)—C(6A)	1.396(4)	1.392(4)
O(1A)—C(20A)	1.393(4)	1.382(4)
O(2A)—C(2A)	1.314(4)	1.312(4)
O(3A)—C(29A)	1.313(4)	1.313(4)
O(4A)—C(43A)	1.321(4)	1.318(4)
C(1A)—N(1A)	1.375(4)	1.366(4)
N(1A)—C(15A)	1.391(4)	1.380(4)
N(2A)—C(35A)	1.299(4)	1.295(4)
N(2A)—C(36A)	1.444(4)	1.447(4)
N(3A)—C(49A)	1.294(4)	1.292(4)
N(3A)—C(50A)	1.440(4)	1.445(4)

Angle	ω/deg	
	2a	**2b**
O(2A)—Co(2)—O(4A)	86.76(9)	87.31(9)
O(2A)—Co(2)—O(3A)	173.04(9)	172.62(10)
O(4A)—Co(2)—O(3A)	89.06(9)	88.52(10)
O(2A)—Co(2)—N(2A)	91.55(10)	91.25(10)
O(4A)—Co(2)—N(2A)	86.48(10)	84.99(10)
O(3A)—Co(2)—N(2A)	93.74(10)	94.45(10)
O(2A)—Co(2)—N(3A)	89.09(10)	88.51(10)
O(4A)—Co(2)—N(3A)	91.98(10)	92.88(11)
O(3A)—Co(2)—N(3A)	85.50(10)	85.62(10)
N(2A)—Co(2)—N(3A)	178.30(11)	177.87(12)
O(2A)—Co(2)—N(1A)	84.29(10)	84.10(10)
O(4A)—Co(2)—N(1A)	170.86(10)	171.19(10)
O(3A)—Co(2)—N(1A)	100.03(10)	100.23(10)
N(2A)—Co(2)—N(1A)	91.91(11)	93.24(11)
N(3A)—Co(2)—N(1A)	89.72(11)	88.84(11)

The ESR spectra of a solution of complex **2b** in toluene (210 K) have a hyperfine structure (HFS) and contain ten HFS lines caused by the interaction of an unpaired electron with the cobalt and nitrogen nuclei (Fig. 2). An analysis of the structure of the spectrum makes it possible to determine the constants of spin density distribution in the chelate fragment of **2b**: a^{N} =15.4 G, a^{Co} = 12.0 G. The temperature rise results in line broadening, indicating an equilibrium in solution shifted toward the structure that includes penoxazinone in the neutral IQ form.

Scheme 3



R = H (**a**), Me (**b**)

The structure of complex **2b** is confirmed by the data of magnetic susceptibility measurements indicating its low-spin electron state. In the solid phase, the effective moment of complex **2b** is 1.93 μ_B and remains almost unchanged in the temperature range from 77 to 298 K. At the same time, the variation of the temperature of a solution of the complex in deuterated toluene from 263 to 333 K is accompanied by reversible changes in the magnetic moment from 1.89 to 2.67 μ_B. This behavior of the complex can be caused by either the valence-tautomeric equilibrium in solution between the low- (S = 1/2) (ISQ) and high-spin (S = 3/2) (IQ) redox isomers of complex **2b**, or its dissociation to the starting components: 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one **3** and bis(salicylaldiminate)-cobalt(II) **4b** (R = Me), whose magnetic moment is 4.36 μ_B (in benzene it is 4.32 μ_B).[25] In order to choose between these two possible mechanisms, we studied the absorption spectra of complex **2b** in the above temperature range.

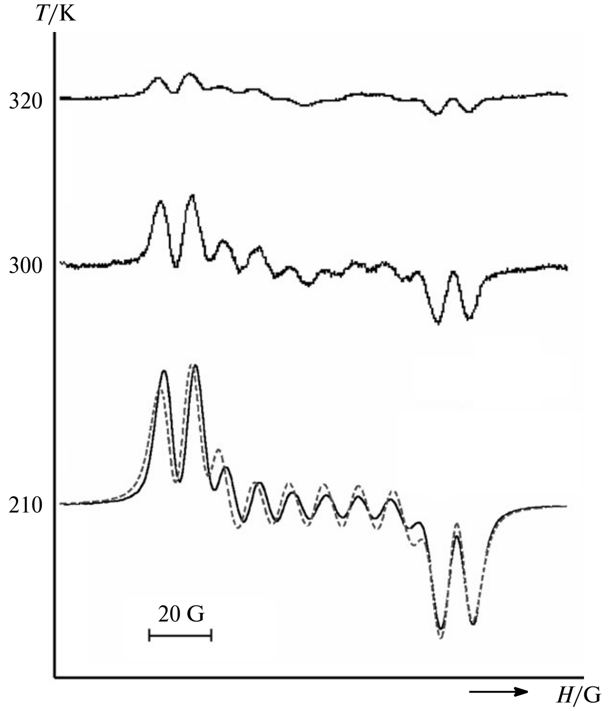


Fig. 2. ESR spectra of compound ISQ-**2b** in a toluene solution at different temperatures (a^N = 15.4 G, a^{Co} = 12.0 G, g = 1.9936) and the simulated ESR spectrum at 210 K (dashes).

The spectrum of complex **2b** in toluene recorded at 283 K (Fig. 3) contains the low-intensity broad band with a maximum at 987 nm ($\varepsilon = 6.5 \cdot 10^2$ L mol^{-1} cm^{-1}) and a shoulder at 935 nm ($\varepsilon = 6.4 \cdot 10^2$ L mol^{-1} cm^{-1}), which can be assigned to the charge-transfer transitions,[26] and the bands at 598 and 397 nm. The absorption with a maximum at 598 nm coincides with the long-wavelength band of free phenoxazinone.

When the temperature of the solution varies from 283 to 328 K, the absorption intensity at 598 nm increases and that at 900—1100 nm decreases. The observed changes are completely reversible (Fig. 4). The presence of two iso-

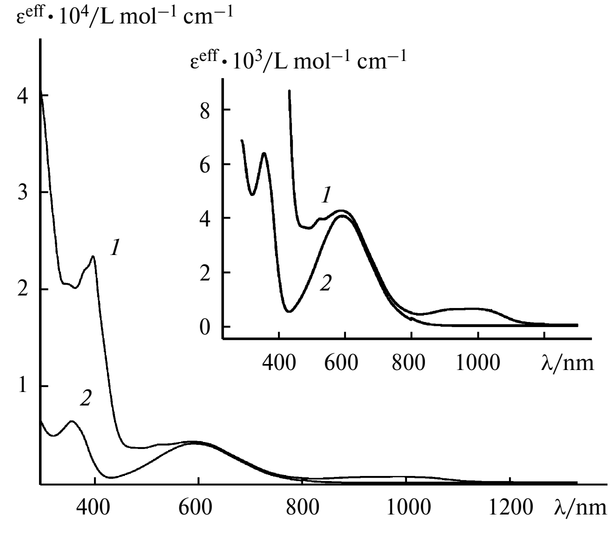


Fig. 3. Absorption spectra of complex **2b** (*1*) and phenoxazinone **3** (*2*) in toluene normalized to the concentration, T = 283 K. Inset: the amplified long-wavelength part of the spectra.

sbestic points indicates that two forms are involved in the dynamic equilibrium. The dissociation products of complex **2b** can be ascribed to one of these forms. The dissociative mechanism of the observed processes is favored by the spectral data presented in Fig. 5 showing that the consecutive dilution of a solution of complex **2b** is accompanied by a decrease in the absorbance at 900—1100 nm and an increase in a range of 598 nm characteristic of the absorption of free phenoxazinone **3**. The stability constant of ISQ-**2b** estimated from the data in Fig. 5 using the dilution method[27] is $9.6 \cdot 10^3$ L mol^{-1}. The thermodynamic parameters of equilibrium ISQ-**2b** $\rightleftharpoons$ **3** + **4b** at 298 K calculated from the temperature dependence of the absorption spectra are the following: $\Delta H = 46\pm1$ kJ mol^{-1}, $\Delta S = 78\pm3$ J mol^{-1} K^{-1}, and $\Delta G = 22.5$ kJ mol^{-1}. The same parameters determined from the data of the temperature dependence of the magnetic moment are $\Delta H = 39$ kJ mol^{-1}, $\Delta S = 77$ J mol^{-1} K^{-1}, and $\Delta G = 16.1$ kJ mol^{-1}.

A probable reason for the discrepancy of the values of ΔG obtained by different methods can be an impurity inclusion of the redox-isomeric rearrangements of complexes **2** to the dynamic process observed in solution.

To explain the processes observed in solutions of complexes **2**, we performed the quantum chemical study of model compounds **2´a** in which the *tert*-butyl groups in positions 4 and 6 of phenoxazinone **3** were replaced by hydrogen atoms.

The calculation results for isolated ligand **3´** in the neutral (IQ) and radical-anion (ISQ) forms are given in Fig. 6. The reduction of the ligand is accompanied by the elongation of the C—O and C—N bonds by 0.03 and 0.05 Å, respectively. These measurements are well consistent with the data obtained for *o*-iminobenzoquinone ligands in similar oxidation states.[28]

Structure **5** on the quartet potential energy surface (PES) corresponds to the associate of bis(salicylaldiminate)cobalt **4a** with neutral form of ligand **3´**. Spin density localization in structure **5** on the metal atom ($q_s^{\text{Co}} = 2.66$) is characteristic of high-spin divalent cobalt (see structure **4a**). Low-spin isomer of adduct **2´a** corresponds to structure LS-**6** on the doublet PES in which the spin density on the metal atom is absent (Table 2) and the single unpaired electron is localized on the redox-active ligand, indicating its radical-anion form. The calculated geometric characteristics of structure LS-**6** well reproduce the X-ray diffraction data for complex **2a** (see Table 1). The low-spin form of adduct LS-**6** is by 11.1 kcal mol^{-1} more preferable than high-spin form HS-**5**, which is consistent with the data of magnetochemical measurements and allows one to expect valence isomerism.

In order to establish the mechanism of a process responsible for the change in the magnetic properties of adduct **2´a**, we searched for minimum-energy crossing point (MECP) between two PES. The calculations resulted

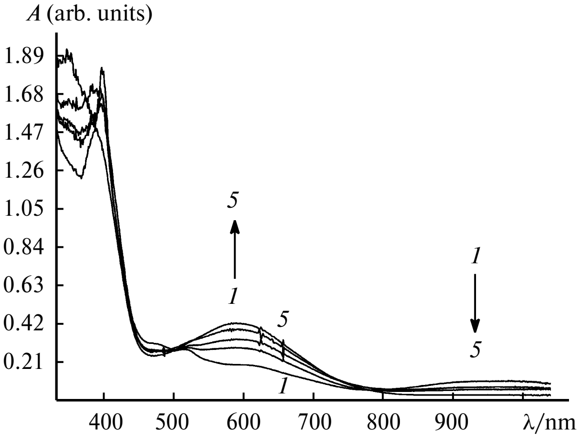


Fig. 5. Absorption spectra of complex **2b** in toluene at the constant product $C_{2b} \cdot l = 1.22 \cdot 10^{-3}$ mol cm L^{-1} at optical pathlength $l = 0.1$ (*1*), 0.5 (*2*), 1.0 (*3*), 2.0 (*4*), and 5.0 cm (5), $T = 293$ K.

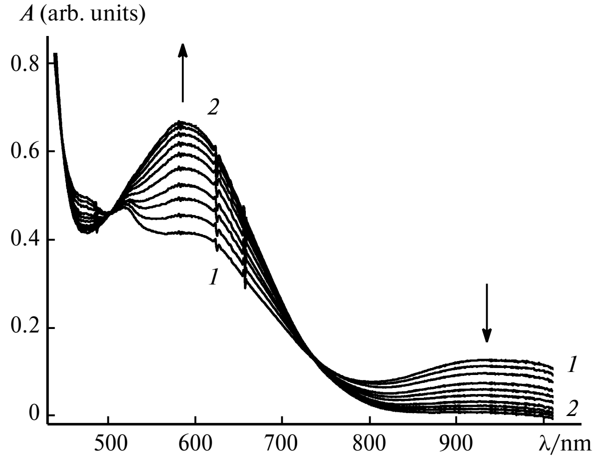


Fig. 4. Absorption spectra of complex **2b** in toluene in the temperature range from 283 (*1*) to 328 K (*2*) with an increment of 5 K, $C_{4b} = 8.32 \cdot 10^{-5}$ mol L^{-1}.

Table 2. Total energy (E_{tot}), stabilization energy (ΔE_{st}), relative energy (ΔE), and spin density on the metal atom (q_s^{Co}) for structures **3´**, **4a**, and **5**—**7** calculated by the DFT B3LYP*/6-311++G(d,p) method

Structure	S	$-E_{\text{tot}}$/au	ΔE_{st}	ΔE	q_s^{Co}
			kcal mol^{-1}		
SQ-**3´**	0	980.7715572	—	—	—
ISQ-**3´**	1/2	980.8446537	—	—	—
4a	3/2	2644.977701	—	—	2.67
HS-**5**	3/2	3625.750513	0.8	11.1	2.66
LS-**6**	1/2	3625.768162	11.9	0	0.04
MECP-**7**	—	3625.747164	−1.3	13.2	—

Note. The stabilization energy (ΔE_{st}) was calculated relatively to isolated molecules of bis(chelate) and phenoxazinone in the neutral form.

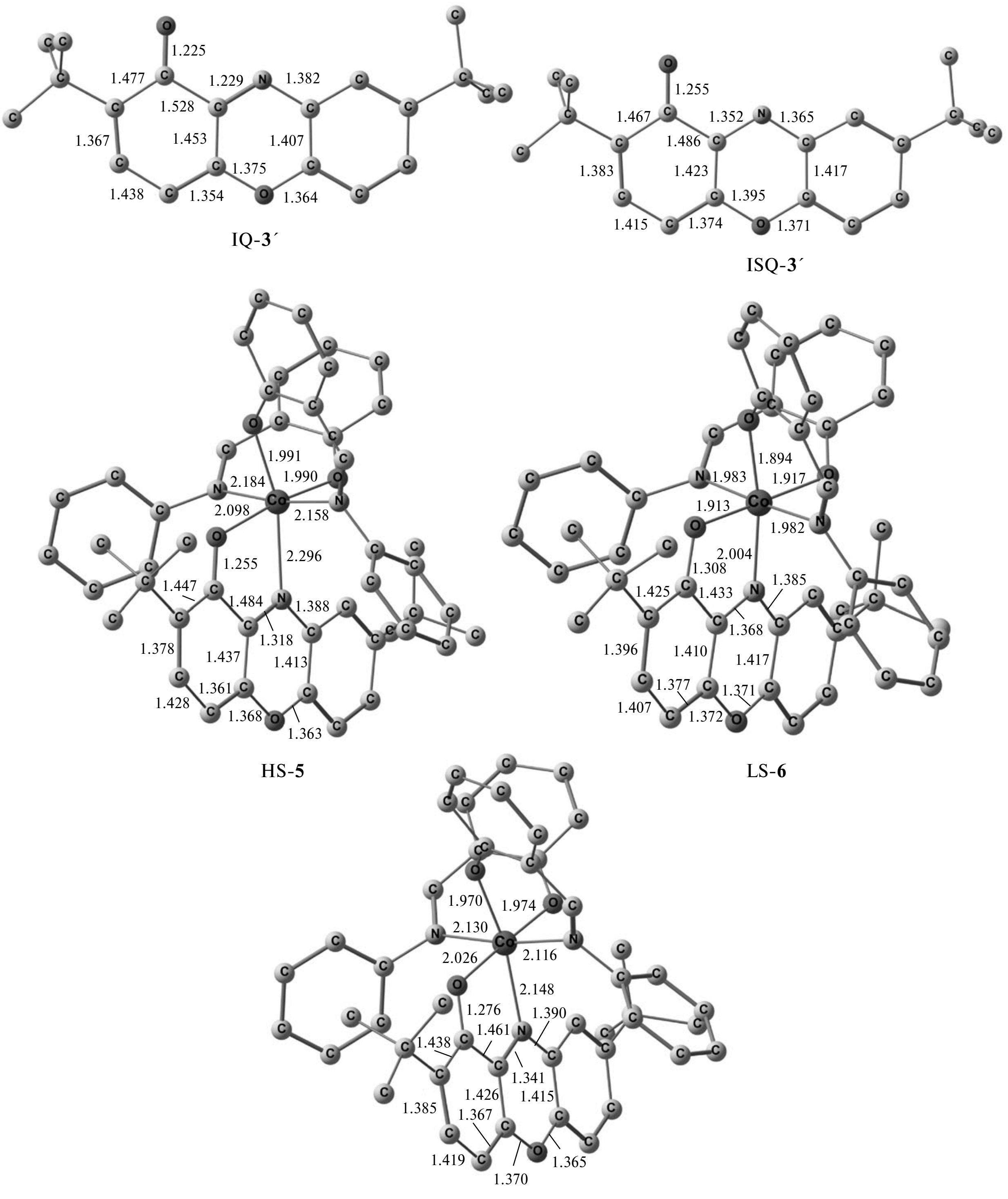


Fig. 6. Geometric characteristics of ligands **3**′ and structures **5**—**7** calculated by the DFT B3LYP*/6-311++G(d,p) method. Hydrogen atoms are omitted. Interatomic distances are given in Å.

in structure MECP-**7** lying by 13.2 kcal mol^{-1} higher than structure LS-**6** (see Table 2). This value somewhat exceeds the experimental values for the valence-tautomeric (VT) rearrangement of the cobalt complexes but is quite attainable. The energy profile of the expected VT rearrangement is presented in Fig. 7.

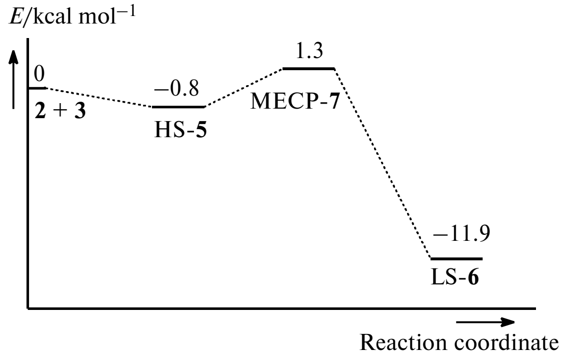


Fig. 7. Energy profile of the intramolecular redox isomerization of complex **2´a**.

It follows from Fig. 7 that the transition of adduct **2´a** from low-spin form LS-**6** to high-spin form HS-**5** through MECP-**7** is poorly probable. This is due to the low stabilization energy of high-spin electromer HS-**5** of adduct **2´a** (0.8 kcal mol^{-1}) and destabilization of MECP-**7** with respect to the starting components by 1.3 kcal mol^{-1}. Thus, it was shown by the quantum chemical calculations that the observed dissociation of adducts **2** to the initial bis(chelate) **4** and phenoxazinone **3** accompanied by a change in the magnetic characteristics is caused by the fact that this process is energetically preferred over the valence-tautomeric rearrangement.

This study showed that synthesized adducts **2** are characterized by the low-spin ground state including the trivalent cobalt atom and phenoxazinone in the radical-monoanion form. The increase in the magnetic moment of solutions of these compounds with the temperature rise is caused by dissociation to the initial molecules rather than by valence tautomerism. To accomplish this type of intramolecular rearrangements, one has to obtain adducts, all forms of which, including the MECP structures, are energetically more favorable than isolated molecules of the bis(chelate) and redox-active ligand. Now we are searching for these structures.

Experimental

Complexes 2 were synthesized by reflux for 30 min of a benzene solution (5 mL) containing bis(salicylaldiminate)cobalt(II) **4** (0.3 mmol) and an equivalent amount of 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one **3**. After the solvent was evaporated and the residue was dried in air, compound **2** was recrystallized from acetonitrile or dimethylformamide. The yields of the complexes were 80—90%.

Compound **2a**. M.p. 138—139 °C. Found (%): C, 73.92; H, 6.84; N, 4.82; Co, 6.75. $C_{54}H_{59}CoN_3O_4$. Calculated (%): C, 74,29; H, 6.81; N, 4.81; Co, 6.75.

Compound **2b**. M.p. 133—134 °C. Found (%): C, 74.51; H, 7.09; N, 4.73; Co, 6.61. $C_{56}H_{63}CoN_3O_4$. Calculated (%): C, 74.65; H, 7.05; N, 4.66; Co, 6.54.

The structures of complexes **2a** and ISQ-**2b** were determined by a direct method and refined using the full-matrix least-squares method for F^2. All calculations were performed using the SHELXTL program package.[29] ESR spectra were obtained on a Bruker EMX Plus 10/12 X-band spectrometer. The hyperfine coupling constants of the ESR spectra were calculated using the Bruker WinEPR SimFonia program package. Absorption spectra were measured on an Agilent 8453 spectrophotometer equipped with a Peltier thermostat. The magnetic moments in solution were measured using a published method[30] on a Bruker Avance 600 NMR spectrometer (600 MHz).

Quantum chemical calculations were performed in the framework of the density functional theory (DFT) by the Gaussian03 program[31] using the 6-311++G(d,p) basis set and B3LYP* modified functional[32] that differs from the standard hybrid B3LYP functional by a decrease in the Hartree—Fock contribution from 0.20 to 0.15. The MECP were calculated using the program code developed by Harvey.[33]

The X-ray diffraction studies of compounds **2a** and **2b** were performed on a SMART APEX II CCD diffractometer (MoKα radiation, graphite monochromator, ω scan mode). The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for F_{hkl}^2. Positions of hydrogen atoms were calculated and refined in the isotropic approximation using the riding model. The main crystallographic data and refinement parameters are given in Table 3. All

Table 3. Main crystallographic data and refinement parameters for structures **2a** and **2b**

Parameter	**2a**	**2b**
Empirical formula	$C_{57}H_{63.50}CoN_{4.50}O_4$	$C_{60}H_{69}CoN_5O_4$
Molecular weight	934.55	983.13
T/K	100	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
$Z(Z')$	4 (1)	8 (2)
a/Å	9.3949(2)	9.9261(11)
b/Å	46.4300(10)	43.970(5)
c/Å	11.8471(3)	24.063(3)
α/deg	90.00	90.00
β/deg	99.8410(10)	90.224(2)
γ/deg	90.00	90.00
V/Å^3	5091.7(2)	10502(2)
d_{calc}/g cm^{-3}	1.219	1.244
μ/cm^{-1}	3.87	3.79
F(000)	1984	4184
$2\theta_{max}$/deg	54	55
Number of measured reflections	31987	106420
Number of independent reflections	10983	24089
Number of reflections with $I > 2\sigma(I)$	6809	13392
Number of refined parameters	608	1293
R_1	0.0612	0.0673
wR_2	0.1676	0.1490
Goodness-of-fit	0.945	0.996
Residual electron density /e Å^{-3}(ρ_{min}/ρ_{max})	−0.543/1.354	−0.782/1.057

calculations were performed using the SHELXTL PLUS program package.[34] The coordinates of atoms and geometric parameters for compounds **2a** and **2b** were deposited with the Cambridge Crystallographic Date Centre (CCDC 947030 and 947031, respectively).

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