

High-Spin Adducts of Redox Active 2,4,6,8-Tetrakis(*tert*-Butyl)phenoxazin-1-One with Tetrahedral Cobalt(II) Complexes

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Abstract—The complex formation between redox active 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one (L) and four-coordinate Co(II) complexes, resulting in six-coordinate adducts (I) (C₇₇H₈₂N₁₂O₅Co) and (II) (C₃₈H₄₁NO₆F₁₂Co) was studied. High-spin structure of the formed cobalt adducts I and II (*hs*-Co^{II}-BQ) was established by X-ray diffraction analysis and magnetochemistry methods. Adducts I and II are stable over a wide temperature range (5–300 K) and are not involved in the redox process giving low-spin adducts (*ls*-Co^{III}-SQ) studied previously.

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INTRODUCTION

Development of the synthetic chemistry of compounds representing molecular magnets is related to the necessity to further develop carriers used for data recording in the memory storage devices. In recent years, the line of research dealing with objects involved in various intramolecular electronic and magnetic interactions has formed and has been intensively developed in coordination chemistry. For transition metal complexes with redox ligands, reversible intramolecular redox isomerism in solution [1–3] and in the solid phase [4–6] and photo- and thermomechanical effects [7, 8] were discovered and investigated. These processes can occur in coordination compounds of transition metals containing so-called non-innocent ligands, which have nearly degenerate electronic states, arising upon a low-barrier thermo- or photostimulated intramolecular electron transfer between the ligand and the transition metal ion.

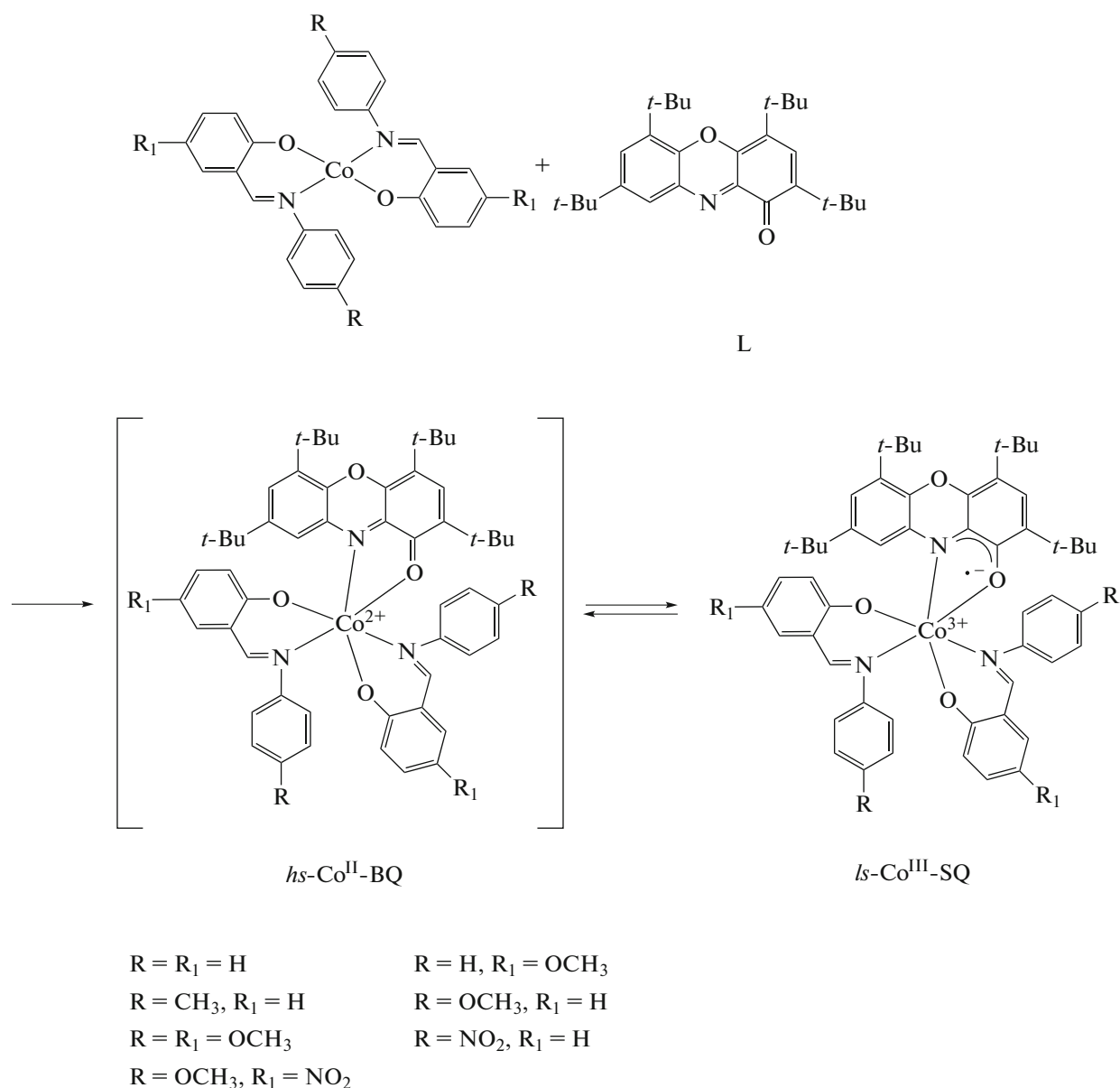
Previously, it was shown that the interaction of high-spin tetrahedral Co(II) bis-azomethine complexes with redox active 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one (L) gives rise to low-spin octahedral adducts (*ls*-Co^{III}-SQ) (Scheme 1). It is possible to obtain extensive ranges of mixed-ligand six-coordinate cobalt complexes by the reaction of redox active 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one with tetrahedral Co(II) bis(salicylaldiminates) on heating in toluene (Scheme 1) [9–11]:

A study of the crystal structure and magnetic properties of the resulting complexes (*ls*-Co^{III}-SQ) showed that they were low-spin radical ion complexes. They were stable and remained invariable over a broad temperature range (5–300 K). This fact supports the assumption of a redox process shifted toward the low-spin form (*ls*-Co^{III}-SQ).

In this study, we developed synthetic routes to and studied the structure and magnetic properties of high-spin six-coordinate adducts (*hs*-Co^{II}-BQ), (I) and (II), formed upon the reaction of redox active 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one (L) and high-spin tetrahedral cobalt complexes with pyrazolonate and trifluoroacetylacetonate ligands, (III) and (IV), respectively.

EXPERIMENTAL

Synthesis of the adduct of bis{3-methyl-1-phenyl-4-[(phenylazo)phenylaminomethylene]pyrazol-5-onate}cobalt(II) with 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one (I). A solution of ligand L (84 mg, 0.2 mmol) in 5 mL of benzene was added to a hot solution of III (164 mg, 0.2 mmol) [1] in 10 mL of benzene, and the mixture was refluxed for 30 min. The solvent was distilled off, and the residue was recrystallized from DMF. The yield of green crystals was 206 mg (83%); mp = 236–237°C. The crystals for X-ray diffraction were grown from DMF.



Scheme 1.

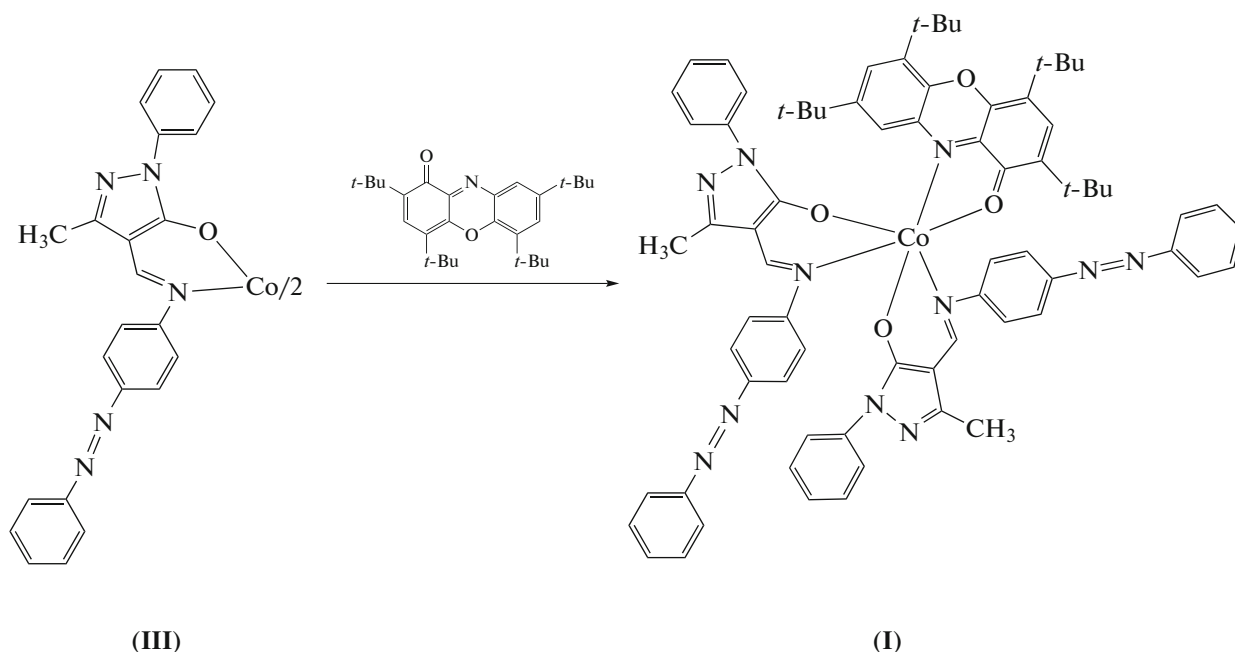
IR (ν , cm^{-1}): 3105 w, 3060 w, 2956 w, 2912 w, 2870 w, 1664 w, 1617 w, 1610 m, 1592 m, 1580 s, 1533 m, 1522 m, 1487 s, 1454 m, 1396 w, 1365 m, 1335 s, 1289 w, 1243 w, 1219 m, 1184 w, 1151 w, 1103 w, 1071 w, 1059 m, 1030 w, 1004 m, 975 w, 927 w, 911 w, 884 w, 854 m, 846 m, 810 w, 791 w, 755 s, 689 s, 654 m, 638 m, 619 m, 607 s, 558 m.

For $\text{C}_{74}\text{H}_{75}\text{N}_{11}\text{O}_4\text{Co}$

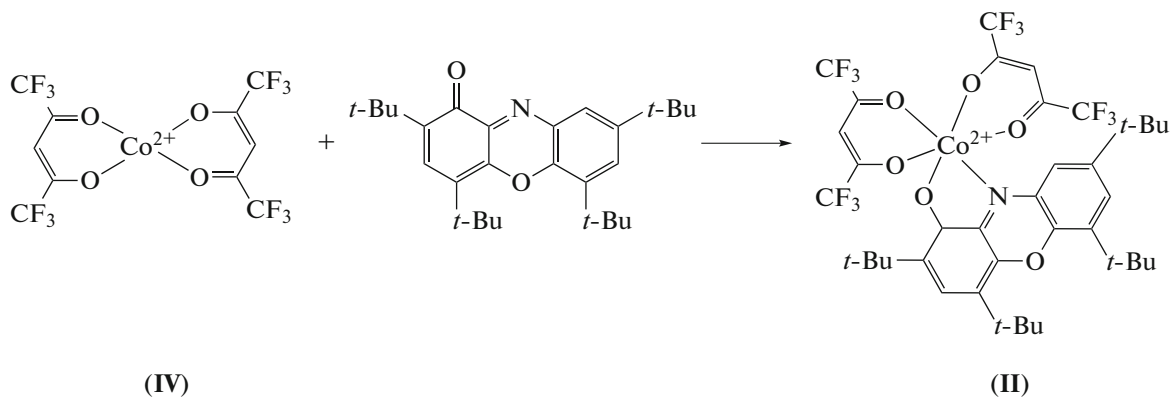
anal. calcd., %: C, 71.60; H, 6.09.
 Found, %: C, 71.49; H, 6.18.

Synthesis of the adduct of bis[(Z)-4,4,4-trifluoro-3-oxo-1-(trifluoromethyl)buten-1-oxy]cobalt with 2,4,6,8-tetrakis(tert-butyl)phenoxazin-1-one (II). For

the preparation of anhydrous Co(II) hexafluoroacetylacetonate, a solution of Co(II) hexafluoroacetylacetonate dihydrate (102 mg, 0.2 mmol) in 6 mL of benzene was refluxed until a benzene–water azeotrope was completely distilled off. Then the solution was cooled down to room temperature, a solution of 2,4,6,8-tetrakis(tert-butyl)phenoxazin-1-one (84 mg, 0.2 mmol) in 3 mL of anhydrous benzene was added, and the mixture was kept for 30 min at this temperature. The solvent was evaporated at room temperature, and the residue was dissolved in 10 mL of hexane. The solution thus formed was filtered, and hexane was evaporated at room temperature. The yield of green crystals of complex $\text{II} \cdot \text{C}_6\text{H}_{12}$ was 160 mg (82%); mp = 183–184°C. The crystals for X-ray diffraction were grown from hexane.



Scheme 2.



Scheme 3.

IR (ν , cm^{-1}): 2968 w, 2914 w, 2873 w, 1638 m, 1600 w, 1581 w, 1556 w, 1528 w, 1474 m, 1459 m, 1389 w, 1366 w, 1345 w, 1306 w, 1251 m, 1196 m, 1141 s, 1095 m, 1035 w, 1006 w, 989 w, 949 w, 926 w, 913 w, 885 w, 837 w, 798 m, 770 w, 757 w, 742 w, 696 w, 666 m, 646 w, 630 w, 585 m, 557 w.

For $\text{C}_{44}\text{H}_{55}\text{NO}_6\text{F}_{12}\text{Co}$

anal. calcd., %:	C, 53.80;	H, 5.72.
Found, %:	C, 53.88;	H, 5.65.

X-ray diffraction data for **I** and **II** were collected on an automated diffractometer (Bruker AXS) using a standard procedure. The structure was solved by the direct method and refined using the least-squares method in the full-matrix anisotropic approximation

for non-hydrogen atoms. Analysis of the difference Fourier electron density maps demonstrated that one phenyl group in the crystal of **I** is disordered over two positions, DMF solvent molecules are disordered over three positions, and one N=N group is disordered over two positions. The H atom positions are calculated geometrically and refined in the riding model. All calculations were carried out using a SHELXTL 6.14 program package. Selected crystallographic data are summarized in Table 1.

The atom coordinates and other parameters of structures **I** and **II** are deposited with the Cambridge Crystallographic Data Centre (nos. 1468781 (**I**), 1403921 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Key crystallographic data and refinement parameters for structures **I** and **II**

Parameter	Value	
	I	II
Molecular formula	C ₇₄ H ₇₅ N ₁₁ O ₄ Co	C ₃₈ H ₄₁ F ₁₂ NO ₆ Co, C ₆ H ₁₄
<i>M</i>	1314.48	980.82
<i>T</i> , K	120	120
System	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i> (<i>Z'</i>)	4 (1)	2 (1)
<i>a</i> , Å	10.8041(12)	13.0757(12)
<i>b</i> , Å	18.583(2)	13.3758(13)
<i>c</i> , Å	37.998(4)	13.8718(14)
α , deg	90	87.449(3)
β , deg	94.104(2)	74.147(2)
γ , deg	90	86.155(2)
<i>V</i> , Å ³	7609.3(15)	2327.8(4)
ρ (calcd.), g cm ⁻³	1.227	1.399
μ , cm ⁻¹	2.87	4.62
<i>F</i> (000)	2980	1018
2 θ _{max} , deg	55	55
Number of measured reflections	45949	17854
Number of unique reflections	17346	10504
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	10117	6582
Number of refined parameters	980	591
<i>R</i> ₁ for <i>I</i> > 2 σ (<i>I</i>) reflections	0.0706	0.0416
<i>wR</i> ₂ for all reflections	0.2103	0.0782
GOOF	1.014	1.006
$\Delta\rho_{\min}/\Delta\rho_{\max}$, e Å ⁻³	-0.851/1.034	-0.598/0.642

RESULTS AND DISCUSSION

In cobalt complexes **I** and **II**, the coordination sphere of the central ion is a distorted octahedron (Fig. 1).

In complex **I** the five-membered metallacycle, Co(1)N(1)C(1)C(2)O(1), occurs in an envelope conformation with the cobalt atom deviating from the plane (the dihedral angle (DA) between the Co(1)N(1)O(1) and N(1)C(1)C(2)O(1) planes is 18.86°), while the six-membered rings have a sofa conformation in which the cobalt atom deviates from the plane (DAs of 12.32° and 10.00°, respectively). In complex **II**, the conformation of the five-membered Co(1)N(1)C(1)C(2)O(1) ring is also an envelope with a slight deviation of the cobalt atom (the DA between the Co(1)N(1)O(1) and N(1)C(1)C(2)O(1) planes is 7.63°). The Co(1)O(5)C(34)C(35)C(36)O(6) and Co(1)O(3)C(29)C(30)C(31)O(4) rings have sofa conformations with a considerable deviation of the cobalt

atom from the ring plane (DAs of 25.16° and 21.04°, respectively).

The bond lengths in **I** (O(1)–C(2), 1.248(4); N(1)–C(1), 1.312(4); C(1)–C(2), 1.476(4) Å) and in **II** (O(1)–C(2), 1.252(3); N(1)–C(1), 1.304(2); C(1)–C(2), 1.489(3) Å) correspond to the iminobenzoquinone (IBQ) form of the 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one ligand L (Table 2; [12]). The Co–O (2.002(2)–2.107(2) Å) and Co–N (2.159(2)–2.252(2) Å) bond lengths in complex **I** are somewhat longer than expected for high-spin compounds and unambiguously attest to the high-spin state of Co²⁺. Meanwhile, the Co–O (2.0254(14)–2.0781(14) Å) and Co–N (2.1643(16) Å) bonds in **II** are shorter than those expected for high-spin adducts and markedly longer than the bonds in the previously synthesized series of low-spin *ls*-Co^{III}–SQ adducts [9]. The difference between the bond lengths with the same-type neighbors (in **II**, 2.6% for the Co–O bond; in **I**, 5.3% for the Co–O bond and 4.3% for the Co–N bond) can

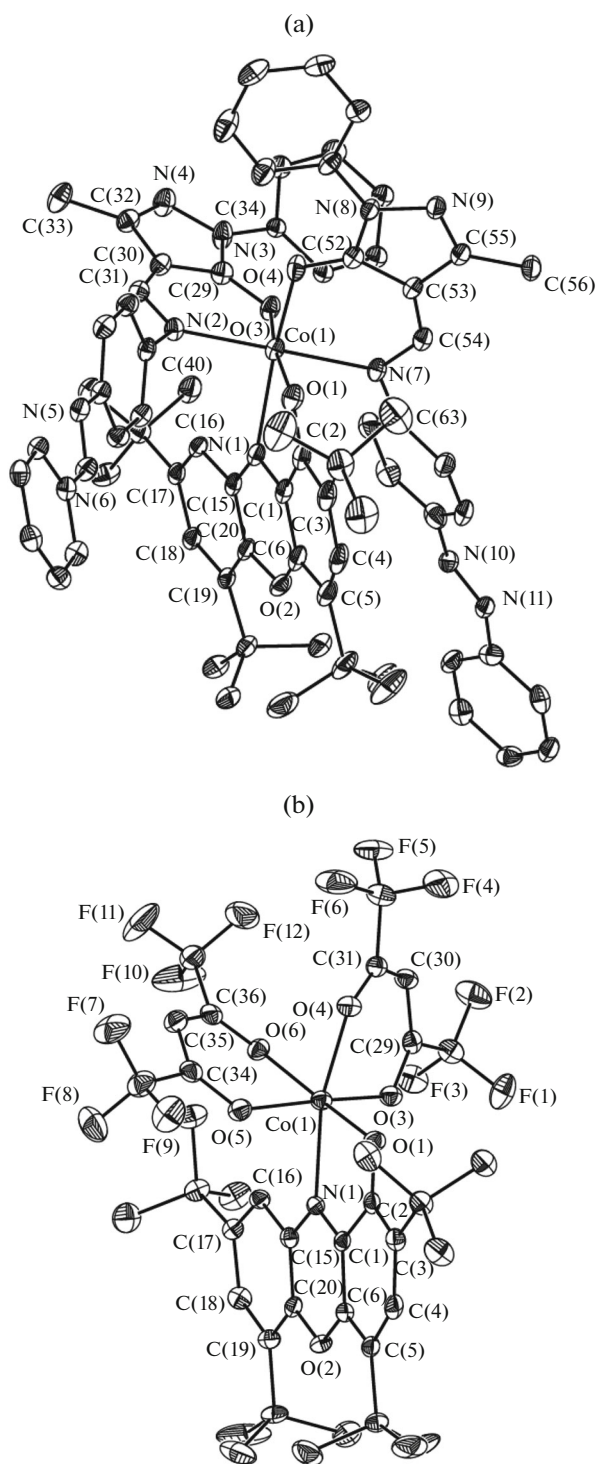


Fig. 1. Molecular structure of complexes (a) **I** and (b) **II** with atoms being represented by thermal ellipsoids of 50% probability.

be attributed to the Jahn–Teller effect in the d^7 ion. The dihedral angles between the N(1)C(1)C(6)O(2) and N(1)C(15)C(20)O(2) planes in the 2,4,6,8-tetrakis(*tert*-butyl)phenoxazin-1-one ligand are

6.44° in **I** and 1.12° in **II**, i.e., this ligand is actually planar.

The observed temperature dependence of the magnetic moment for the high-spin octahedral complexes

Table 2. Selected bond lengths (Å) and angles (deg) of complexes **I** and **II**

<i>d</i> , Å			
I		II	
Co(1)–O(1)	2.107(2)	Co(1)–O(3)	2.0254(14)
Co(1)–O(3)	2.002(2)	Co(1)–O(1)	2.0472(13)
Co(1)–O(4)	2.038(3)	Co(1)–O(5)	2.0519(14)
Co(1)–N(1)	2.252(3)	Co(1)–O(4)	2.0683(14)
Co(1)–N(2)	2.159(3)	Co(1)–O(6)	2.0781(14)
Co(1)–N(7)	2.194(3)	Co(1)–N(1)	2.1643(16)
O(1)–C(2)	1.248(4)	O(1)–C(2)	1.252(2)
N(1)–C(1)	1.312(4)	N(1)–C(1)	1.304(2)
N(1)–C(15)	1.388(4)	N(1)–C(15)	1.391(2)
N(2)–C(31)	1.303(3)	O(2)–C(20)	1.384(2)
N(2)–C(40)	1.421(4)	O(2)–C(6)	1.384(2)
O(2)–C(6)	1.375(4)	O(3)–C(29)	1.258(2)
O(2)–C(20)	1.380(4)	O(4)–C(31)	1.244(2)
O(3)–C(29)	1.288(4)	O(5)–C(34)	1.253(2)
O(4)–C(52)	1.270(3)	O(6)–C(36)	1.258(2)
N(7)–C(54)	1.306(4)		
N(7)–C(63)	1.422(4)		
<i>ω</i> , deg			
I		II	
N(1)Co(1)O(3)	104.65(10)	O(3)Co(1)O(1)	101.39(6)
N(1)Co(1)O(4)	157.99(10)	O(3)Co(1)O(5)	169.95(6)
N(1)Co(1)N(2)	92.69(10)	O(1)Co(1)O(5)	86.30(6)
N(1)Co(1)N(7)	86.95(10)	O(3)Co(1)O(4)	88.92(6)
N(1)Co(1)O(1)	73.34(10)	O(1)Co(1)O(4)	90.54(5)
N(2)Co(1)O(4)	88.04(8)	O(5)Co(1)O(4)	97.55(6)
N(2)Co(1)N(7)	179.25(12)	O(3)Co(1)O(6)	87.27(6)
N(2)Co(1)O(3)	91.38(10)	O(1)Co(1)O(6)	169.54(6)
O(1)Co(1)O(4)	84.71(10)	O(5)Co(1)O(6)	85.81(6)
O(1)Co(1)N(2)	96.63(10)	O(4)Co(1)O(6)	83.71(5)
O(1)Co(1)N(7)	83.90(10)	O(3)Co(1)N(1)	86.61(6)
O(1)Co(1)O(3)	171.81(9)	O(1)Co(1)N(1)	77.14(6)
O(3)Co(1)N(7)	88.08(10)	O(5)Co(1)N(1)	88.84(6)
O(3)Co(1)O(4)	97.32(8)	O(4)Co(1)N(1)	165.78(6)
O(4)Co(1)N(7)	92.52(10)	O(6)Co(1)N(1)	109.53(6)

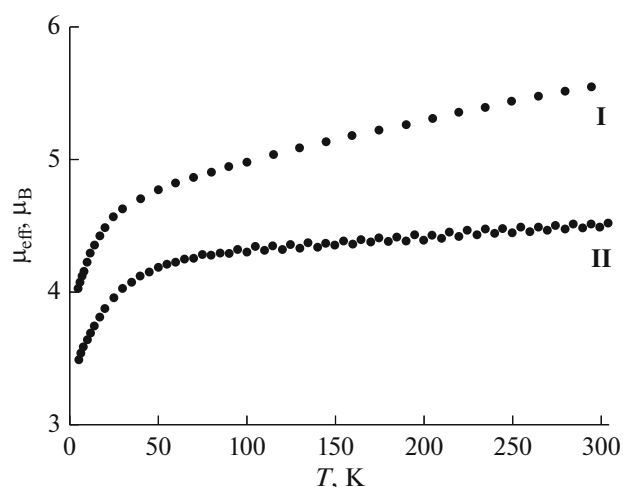


Fig. 2. Dependence of $\mu_{\text{eff}}(T)$ for high-spin octahedral complexes I and II in the 5–300 K temperature range.

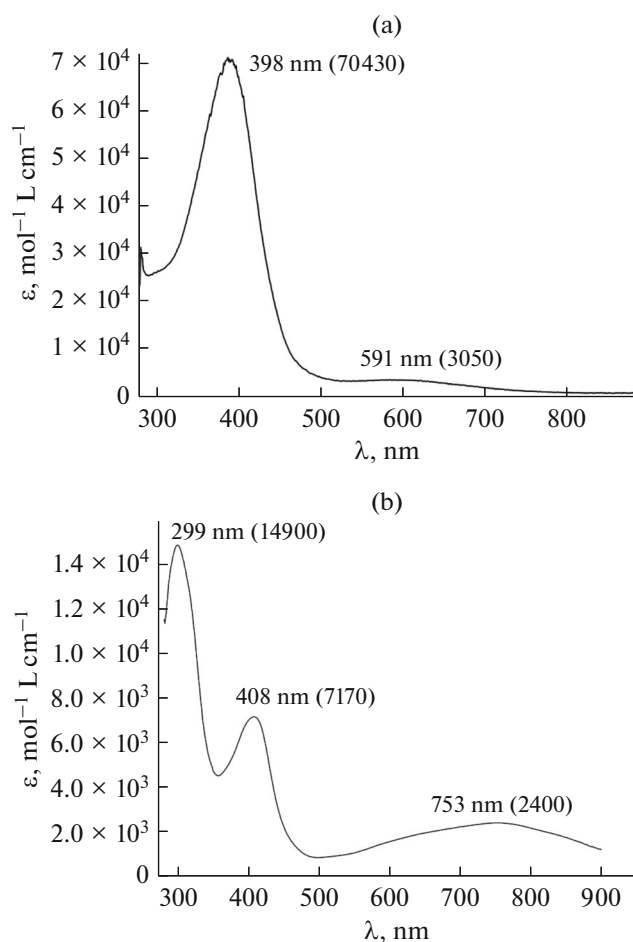


Fig. 3. Absorption spectrum of complexes (a) I and (b) II in toluene at 300 K.

I and II varies in the usual ranges (4.7–5.2 μ_B) typical of high-spin Co(II) complexes (Fig. 2) [13].

The cobalt complexes I and II we synthesized contain similar metallacycles and their magnetic and UV-spectral characteristics (Fig. 3) differ substantially from those of the low-spin octahedral adducts described previously [9–11]. It was found that the ligand environment of the cobalt complexes has a crucial influence on the structure of the adducts (redox isomerism). Enhancement of the electron-withdrawing properties of the ligands induces transition from the low-spin radical ion *ls*-Co^{III}-SQ form to high-spin *hs*-Co^{II}-BQ form, which apparently opens up the synthetic possibility of constructing valence tautomeric complexes with diverse magnetic properties.

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