

Investigation of cobalt (1,10-phenanthroline)-bis-(3,6-di-*tert*-butyl-*o*-benzosemiquinolate) by X-ray diffraction, IR and ESR spectroscopy, magnetochemistry, and precision calorimetry

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The bistable cobalt complex containing two symmetrical 3,6-di-*tert*-butyl-*o*-benzoquinone and one 1,10-phenanthroline moieties as ligands (**1**) was synthesized. Complex **1** was isolated in the individual state and characterized by IR and ESR spectroscopy, X-ray diffraction, magnetochemical studies, and precision calorimetry. A change in temperature causes the reversible metal–ligand electron transfer and spin crossover (redox isomerism) in complex **1** in the crystalline state. The redox-isomeric transformation at ~250 K is accompanied by the phase transition. The structural study at two temperatures confirmed the changes in the molecular and crystal structure associated with the redox-isomeric transformation.

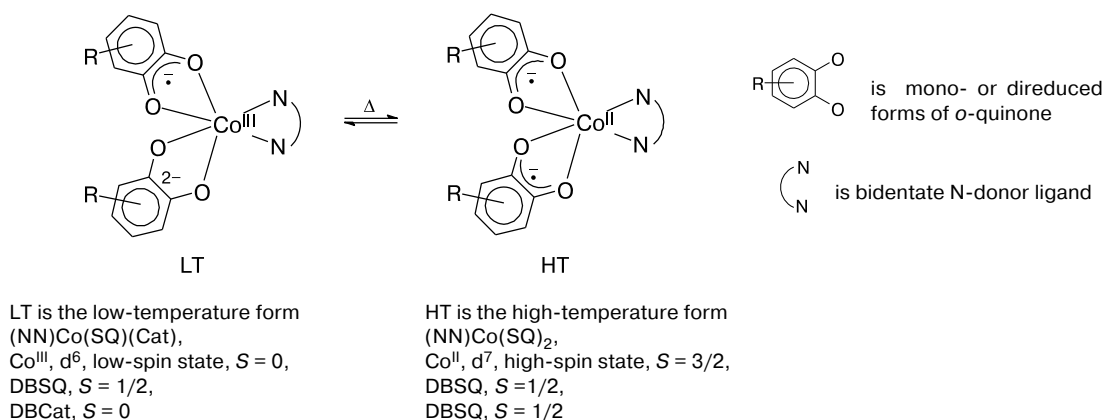
Key words: redox isomerism, *o*-semiquinone, cobalt complex, IR spectroscopy, ESR spectroscopy, magnetic properties, X-ray diffraction study, precision calorimetry.

The redox isomerism, *viz.*, the reversible intramolecular ligand–metal electron transfer accompanied by a change in the spin multiplicity (Scheme 1), in the solid state was discovered for the first time for cobalt bis-*o*-semiquinone complexes.^{1–3}

More recently, comprehensive investigations of this class of compounds have been performed:

1) the influence of the nature of neutral ligands⁴ and solvent molecules⁵ on the equilibrium of the redox isomerism in the solid state was revealed, which makes it

Scheme 1



DBSQ and DBCat are di-*tert*-butyl-*o*-benzosemiquinone and -catecholate, respectively.

possible to synthesize compounds with a desired phase transition temperature ($T_{1/2}$);

2) the photodynamics of redox-isomeric transitions was studied in detail, and methods for the detection and identification of the excited metastable state were examined;^{6,7}

3) the influence of the composition of the complexes and the nature of the ligands on the hysteresis width in the temperature dependence of μ_{eff} was analyzed;⁸

4) based on the temperature dependence of the heat capacity,⁹ it was shown that redox-isomeric transformations are accompanied by the phase transition (λ transition), which can be induced also by electromagnetic radiation,¹⁰ pressure,¹¹ magnetic field,¹² and chemical action (pH),¹³ the temperature and the energy of the transition being dependent on the nature of the *o*-quinone ligand;^{14,15}

5) new types of redox-isomeric cobalt complexes, *viz.*, mono-*o*-semiquinone complexes¹⁶ and dinuclear mixed-valence complexes, were synthesized;¹⁷

6) nanosized redox-isomeric cobalt complexes¹⁸ and complexes immobilized on gold nanoparticles,¹⁹ redox-isomeric cobalt complexes with *o*-semiquinone ligands having liquid-crystalline properties,^{20,21} and polymeric redox-isomeric cobalt complexes²² were prepared;

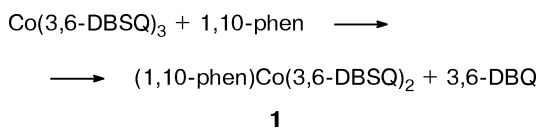
7) the photo(thermo)mechanical effect was found for single-crystal samples of the complex (bpy)Co(3,6-DBSQ)₂.¹

This class of compounds has attracted great interest due primarily to the fact that these compounds show promise as new photoactive magnetic materials.⁷

Looking forward to developing thin-film photomagnetic materials for molecular devices with the use of bistable cobalt compounds, in the present study we synthesized solvent-free²³ cobalt (1,10-phenanthroline)-bis-(3,6-di-*tert*-butyl-*o*-benzoquinolate) (**1**).

Complex **1** was synthesized by the reaction of cobalt tris-semiquinolate with 1,10-phenanthroline (1,10-phen) (Scheme 2).

Scheme 2



3,6-DBQ is 3,6-di-*tert*-butyl-*o*-benzoquinone

Crystals suitable for X-ray diffraction were isolated from diethyl ether.

The IR spectrum of complex **1** (Fig. 1) in the fingerprint region (400–2000 cm^{-1}) is typical of semiquinone complexes. This spectrum is a superposition of the spectra of the ligands and is characterized by intense bands at 1450 cm^{-1} corresponding to stretching vibrations of the carbon–oxygen one-and-a-half bond. The near-IR re-

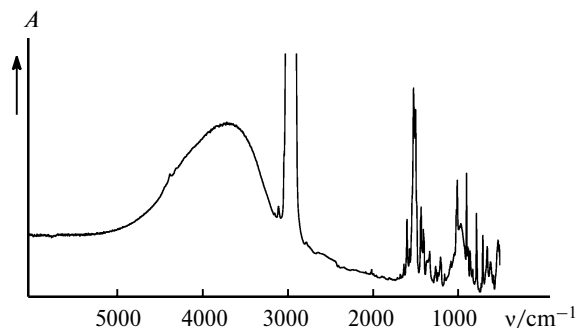


Fig. 1. Spectrum of complex **1** in the IR and near-IR regions (Nujol mulls).

gion shows an intense band at 3626 cm^{-1} (2760 nm) assigned to the Cat \rightarrow SQ charge transfer. In addition, there is an electronic transition band at 900 cm^{-1} , which often attends the Cat \rightarrow SQ charge-transfer band.²⁴

The ESR spectrum of a powder of complex **1** strongly depends on the temperature (Fig. 2). At 130 K, this is the anisotropic spectrum with the axial symmetry of the g tensor: $g_{\perp} = 1.9951$, $g_{\parallel} = 2.0143$. An increase in the temperature is accompanied by a spectral line broadening and a decrease in the integrated intensity. At $T > 270$ K, the signal in the spectrum completely disappears. The same situation has been observed earlier for redox-isomeric complexes¹ and has been explained by a decrease in the fraction of the low-temperature form upon heating.

The temperature dependence of the magnetic moment of complex **1** is shown in Fig. 3. At temperatures below ~ 10 K, the magnetic moment decreases to 1.11 μ_{B} (2.0 K) due, apparently, to intermolecular exchange interactions. In the temperature range from ~ 10 to ~ 220 K, the magnetic moment gradually and monotonically increases from 1.72 to 2.28 μ_{B} , and then a sharp jump occurs in the range of ~ 250 – 300 K (for example, in the temperature range of 250–260 K, the magnetic moment increases from 2.53 to 3.35 μ_{B}). At 360 K, the magnetic moment reaches 4.66 μ_{B} . A temperature hysteresis is absent. The S-shaped temperature dependence of the magnetic moment is typical for

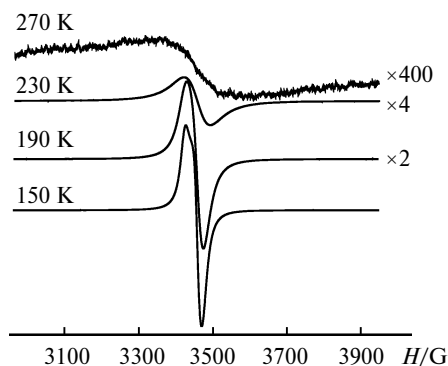


Fig. 2. Temperature dependence of the ESR spectrum of complex **1** (polycrystalline sample).

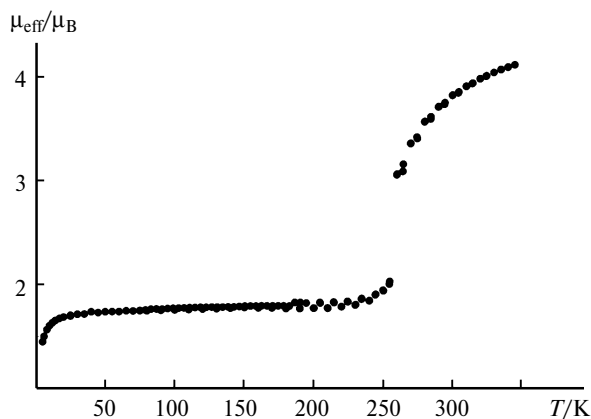


Fig. 3. Temperature dependence of the magnetic moment of complex **1**.

redox-isomeric complexes and compounds, in which the spin multiplicity of the central metal atom changes with temperature (spin crossover).

The temperature dependence of the heat capacity of complex **1** in the range of 5–320 K was studied by precision adiabatic vacuum calorimetry (Fig. 4).

In the temperature range from 5 to 214 K, the heat capacity monotonically increases. In the range from 214 to 234 K, the anomalous deviation from the typical curve is observed (the maximum deviation $\Delta C_p^\circ = 30 \text{ J mol}^{-1} \text{ K}^{-1}$ is observed at $T = 225.4 \text{ K}$). The enthalpy of the anomaly is $301 \pm 10 \text{ J mol}^{-1}$. In the temperature range of 240–281 K, a sharp increase in the heat capacity occurs due to the redox-isomeric transition. The temperature, at which the heat capacity in the transition range has the highest value ($C_p^\circ = 2360 \text{ J mol}^{-1} \text{ K}^{-1}$), is $254.5 \pm 0.1 \text{ K}$. The enthalpy of the transformation evaluated by the continuous energy supply technique based on three experiments is $6.320 \pm 0.079 \text{ kJ mol}^{-1}$, and the entropy is $24.8 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

The standard thermodynamic functions of complex **1** in the temperature range from $T \rightarrow 0$ to 320 K were calcu-

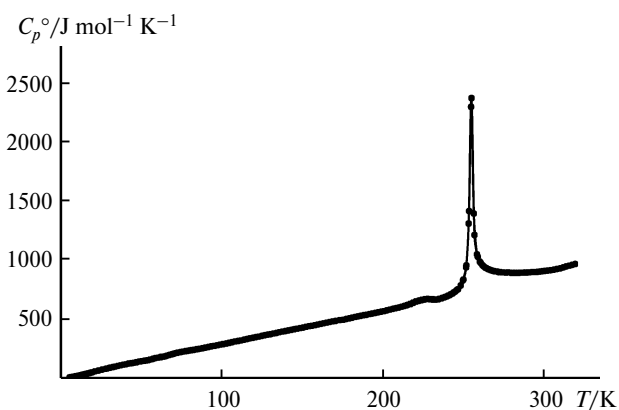


Fig. 4. Temperature dependence of the heat capacity of complex **1**.

lated from the above data. The calculation procedure was described in detail in the study.²⁵ At 298.15 K and ambient pressure, the following values of the thermodynamic functions were obtained: $C_p^\circ = 946.4 \text{ J mol}^{-1} \text{ K}^{-1}$, $H^\circ(T) - H^\circ(0) = 143.4 \text{ kJ mol}^{-1}$, $S^\circ(T) = 900.8 \text{ J mol}^{-1} \text{ K}^{-1}$, $G^\circ(T) - G^\circ(0) = -125.2 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

According to the X-ray diffraction data, the inner coordination sphere of complex **1** is nearly octahedral. At 240 K, the angles at the cobalt atom, O(2)–Co–O(2) and N(1)–Co–O(1), are 176.42 and 172.47°, respectively; the corresponding angles at 293 K are 162.53 and 171.39°. The *o*-quinone ligands are bent along the O–O line. The bending angle is 14.82 and 18.75° at 293 and 240 K, respectively; in addition, at 240 K the planes of the chelate unit O(1)–C(1)–C(8)–O(2) and the aromatic ring of the ligand are twisted (3.62°). The molecular structure and the atomic numbering scheme for the inner coordination sphere in complex **1** are presented in Fig. 5. The bond lengths characterizing the oxidation state of the metal atom and the ligands, as well as selected bond angles, are listed in Table 1.

The bond lengths and the O(1)–Co–O(2) angle are given only for one of the quinone ligands, because the structure refinement was carried out in the space group *C2/c*. Since the Co atom lies in a special position on a twofold axis passing through the Co atom and the center of the Phen molecule, the SQ ligands are identical. By assuming the possibility of the redox-isomeric transition accompanied by a change in the oxidation state of the metal atom $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ and the reduction of one of the semiquinone ligands to the catecholate ligand, we attempted to decrease the symmetry of the crystal structure to

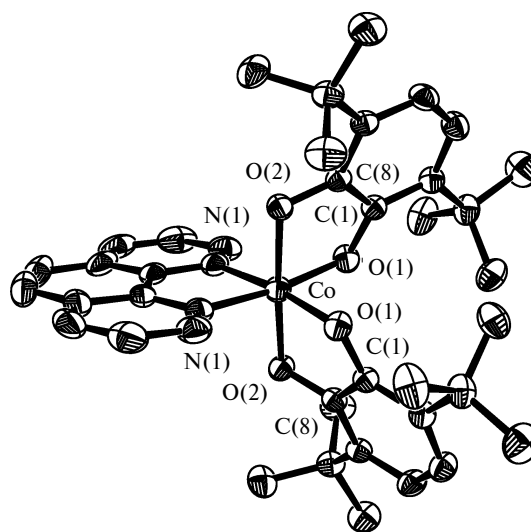


Fig. 5. Molecular structure and the atomic numbering scheme for the inner coordination sphere of complex **1** at 240 K (displacement ellipsoids are drawn at the 30% probability level). The hydrogen atoms are not shown.

Table 1. Selected bond angles (d) and the bond angle (ω) in the inner coordination sphere of complex **1** at 240 and 293 K

Parameter	240 K	293 K
Bond length	$d/\text{\AA}$	
Co—O(1)	1.856	2.013
Co—O(2)	1.868	1.991
Co—N(1)	1.943	2.073
C(1)—O(1)	1.334	1.290
C(8)—O(2)	1.321	1.289
Angle	ω/deg	
O(1)—Co—O(2)	87.000	80.270

exclude the symmetry relation between the SQ ligands. However, although the X-ray diffraction data were collected in the full sphere of reciprocal space ($\pm h, \pm k, \pm l$), the structure refinement in the space group Cc led to a higher error in the determination of the bond lengths and the distortion of the geometry of some moieties and did not reduce the R factor.

At 240 K, the bond lengths in the nearest environment of the cobalt atom are, on the whole, smaller than those at 293 K, which confirms the change in the charge on the cobalt atom from 3+ at 240 K to 2+ at 293 K. The C—O bond lengths characterizing the effective charge on the quinone ligand are larger at 240 K than at 293 K. At the low temperature, these values are at the lower limit of the

range 1.31–1.35 Å characteristic of the coordination of the catecholate form. At room temperature, these values correspond to the upper limit of the range 1.27–1.31 Å typical of the coordinated radical anion.²⁶ In addition, the O(1)—Co—O(2) bond angle in the low-temperature form is substantially larger than that in the high-temperature form.²⁷

Therefore, the structural data confirm the change in the charge distribution in complex **1** with a change in the temperature.

The crystal packing of complex **1** is, on the whole, typical of such complexes and changes only slightly with temperature. The unit cell parameters of complex **1** and its analogs are given in Tables 2 and 3.

As in the most of the related complexes,^{1–3} the crystal packing of complex **1** is based on a one-dimensional motif composed of the planes of neutral N-donor ligands that form a ladder framed by *o*-quinone moieties (Fig. 6).

It should be noted that complexes of the composition (1,10-phen)Co(SQ)₂, *viz.*, analogs of **1**, have been characterized earlier. In particular, the complex (1,10-phen)-Co(3,5-DBSQ)₂, in which 3,5-di-*tert*-butyl-*o*-benzosemiquinone serves as the SQ ligand, and its solvates with toluene (**2**) and chlorobenzene (**3**) were described (see Ref. 3). In the latter study, it was also shown that the method of the preparation of the sample plays a key role in its magnetic properties. In particular, the toluene solvate shows a sharp change in the magnetic properties. Thus, in the temperature range of 220–260 K the low-temperature (LT) form is almost completely transformed into the high-temperature (HT) form. The chlorobenzene solvate **3** shows a slower change in the magnetic moment with increasing temperature, although the limiting values are equal to those found for the toluene solvate. The non-solvated samples have quite different magnetic properties in spite of the identical composition. Thus, the sample prepared by recrystallization from methylcyclohexane has a low magnetic moment, which remains virtually unchanged in the temperature range of 20–330 K, whereas the sample prepared by grinding the toluene solvate followed by the removal of toluene *in vacuo* undergoes the redox-isomeric transition strongly extended in the temperature range. It should be noted that the complete trans-

Table 2. Unit cell parameters of complex **1** at 240 and 293 K

Parameter	240 K	293 K
Space group	$C2/c$	$C2/c$
$a/\text{\AA}$	10.6069(9)	10.601(2)
$b/\text{\AA}$	30.644(3)	31.706(8)
$c/\text{\AA}$	12.1996(13)	12.201(3)
α/deg	90	90
β/deg	113.124(6)	114.515(14)
γ/deg	90	90

Table 3. Unit cell parameters of the adducts of 3,5-DBSQ with different solvent molecules

Parameter	(<i>o</i> -phen)Co(3,5-DBSQ) ₂ ·Tol (2)	(<i>o</i> -phen)Co(3,5-DBSQ) ₂ ·PhCl (3)
Space group	$P2_1/c$	$P2_1/c$
$a/\text{\AA}$	10.425(3)	10.444(2)
$b/\text{\AA}$	32.226(8)	32.852(9)
$c/\text{\AA}$	13.454(4)	13.437(3)
α/deg	90	90
β/deg	111.39(2)	110.92(2)
γ/deg	90	90

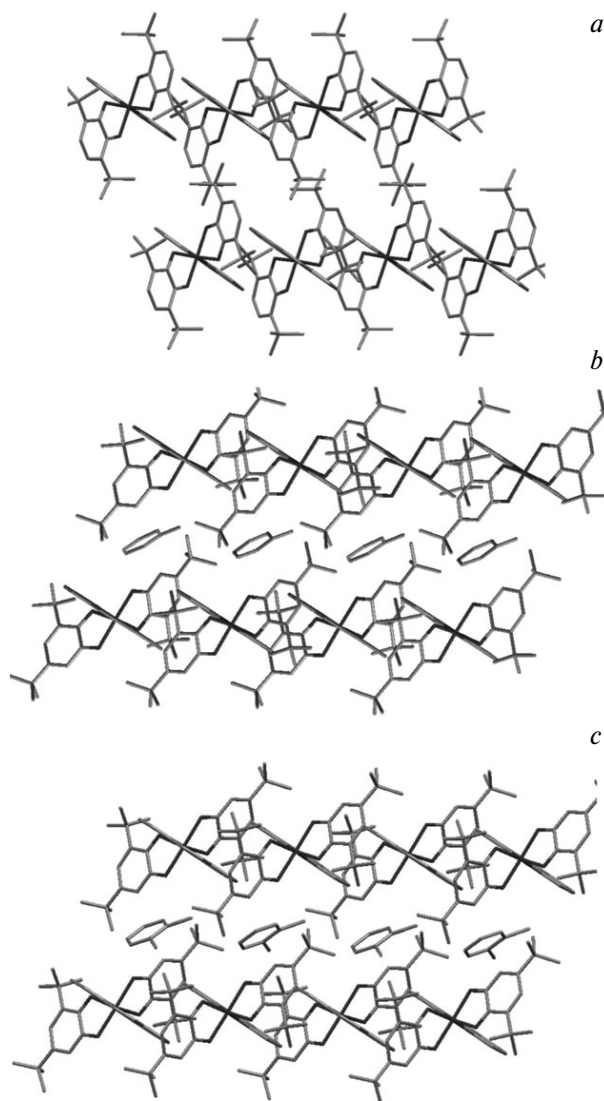


Fig. 6. Side views of the molecular chains of complex **1** (a) and its analogs **2** (b) and **3** (c) along the *b* axis of the unit cell.

formation is not achieved at either low or high temperatures.

The spectroscopic and magnetic properties of the complex (1,10-phen)Co(3,6-DBSQ)₂·C₆H₆ were documented.²³ In particular, based on the temperature dependence of the absorption spectrum, the transition temperature in a toluene solution was evaluated as $T_{1/2} = 265$ K. The intensity of the Cat → SQ charge-transfer band of a powder of the complex in the near-IR region (~2400 nm) depends on the temperature. According to the results of the study,²³ the magnetic moment monotonically changes from 1.78 μ_B at 5 K to 6.04 μ_B at 340 K with a slight splash at ~250 K.

A substantial difference in the crystal packing of **1** and its analogs is that there are no solvent molecules located between the ladders formed by the phenanthroline ligands

in the structure of **1**. This is clearly seen in Fig. 7, which shows projections of two adjacent molecular chains.

In the crystal structure of **1**, the planes of the adjacent *o*-phenanthroline moieties in the chains are parallel, and the distances between these moieties are equal (3.359 and 3.462 Å at 240 and 293 K, respectively). In complexes **2** and **3**, the planes of the adjacent *o*-phen ligands are non-parallel (the alternate *o*-phen ligands are parallel to each other); the angle between the adjacent planes is 2.19° (**2**) and 2.37° (**3**). The distances between the parallel alternate planes are 6.854 Å (one-half is 3.427 Å) in **2** and 6.926 Å (one-half is 3.463 Å) in **3** (room temperature).

The changes in the unit cell parameters associated with the redox-isomeric process in compound **1** are somewhat different from those in **2**. For the crystals of **1**, an increase in the temperature leads to an elongation of the *b* axis by 3.5% and an increase in the angle β by 1.2%, whereas an increase in the temperature influences the parameters *b* and *c* in **2** (an increase by 2.6 and 3.0%, respectively). These slight structural differences are reflected in the temperature and the steepness of the transition, but do not lead to such radical changes as the removal of the solvent from compound **2** (grinding and removal *in vacuo* or recrystallization of **2** from methylcyclohexane).

In essence, the μ_{eff}–*T* curve characterizes the redox-isomeric transformation (the transformation of the LT form into the HT form), because the magnetic moment is the sum of the magnetic moments of different forms with account for their molar fractions. The temperature ranges of the transitions in compounds **1**, **2**, and **3** are 250–350, 200–260, and 160–300 K, respectively. The thermodynamic characteristics of the transformation from the LT form into the HT form in a polycrystalline sample of **2** estimated from the data on the magnetic susceptibility³ were as follows: Δ*H* = 83.7 kJ mol^{−1}, Δ*S* = 345 J mol^{−1} K^{−1}. The authors of the cited study admitted that these values are unrealistically large because this change in the entropy should correspond to the impossible change in the number of the degrees of freedom by 10¹⁸. In another study,²⁸ these authors reported the thermodynamic characteristics of the same process but in solution (toluene-*d*₈), which were also estimated from the data on the magnetic susceptibility: Δ*H* = 26.77 kJ mol^{−1}, Δ*S* = 118.1 J mol^{−1} K^{−1}. The authors believed that the latter values are typical of redox-isomeric processes in such cobalt complexes.

The redox potentials of 3,5- and 3,6-DBQ are only slightly different. Hence, it can be expected that the enthalpy and the entropy for the equilibrium of the redox isomerism for complexes **1** and **2** have similar values. In the case under consideration, Δ*H* and Δ*S* calculated from the magnetochemical data for complex **1** in solution (the Evans method) have similar values: Δ*H* = 23.3 kJ mol^{−1}, Δ*S* = 91.3 J mol^{−1} K^{−1}.

The values of Δ*H* and Δ*S* estimated by precision adiabatic vacuum calorimetry (6.32 kJ mol^{−1} and 24.8 J mol^{−1} K^{−1},

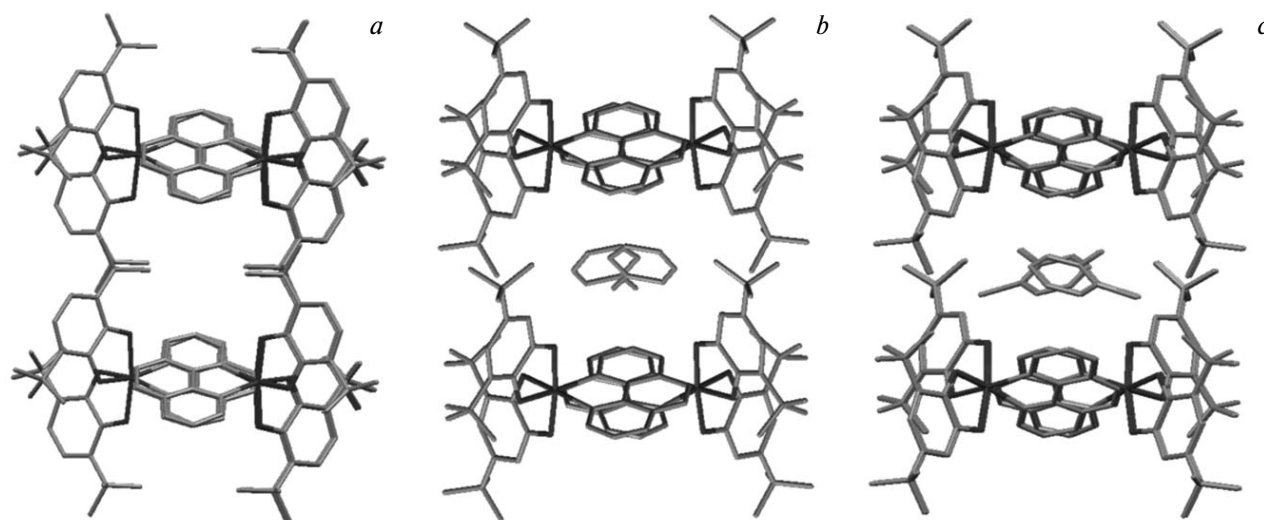


Fig. 7. Views along the molecular chains of complex **1** (a) and its analogs **2** (b) and **3** (c) (views along the ladder consisting of phenanthroline ligands or along the *c* axis).

respectively) are substantially smaller. This is associated with the fact that this method deals with the energetics of the overall process involving both the redox isomerism and the attendant rearrangement of the crystal lattice, whereas magnetochemical measurements in solution characterize only the redox-isomeric transformation. Therefore, the enthalpy and the entropy of the rearrangement of the crystal lattice have an opposite sign, and the lattice structure is more favorable in enthalpy at the high temperature than at the low temperature. Nowadays, it is difficult to adequately explain the factors responsible for the different signs of the enthalpies and entropies of the redox isomerism and the rearrangement of the crystal lattice. However, the same relation is observed also for the complex (bpy)Co(3,6-DBSQ)₂ (**4**). Thus, the enthalpies and entropies determined by precision adiabatic vacuum calorimetry are 15.0 kJ mol⁻¹ and 48.2 J mol⁻¹ K⁻¹, respectively, whereas, the corresponding parameters evaluated by the Evans method are 22.4 kJ mol⁻¹ and 71.3 J mol⁻¹ K⁻¹.

To sum up, we synthesized for the first time the complex (*o*-phen)Co(3,6-DBSQ)₂ without solvent molecules in the crystalline state. Studies by ESR spectroscopy and magnetochemical methods showed that the complex undergoes the redox-isomeric transformation in the temperature range of 250–350 K. The X-ray diffraction data confirm the change in the oxidation state of the cobalt atom and the *o*-quinone ligands. The reversible redox-isomeric reaction is accompanied by the phase transition in the temperature range of 240–280 K. The thermodynamic parameters of the phase transition were determined.

Experimental

Spectroscopic, magnetochemical, and calorimetric studies. The ESR spectra were recorded on a Bruker EMX instru-

ment equipped with a temperature unit. The IR spectra were measured on a FSM 1201 Fourier-transform infrared spectrometer. Magnetochemical measurements were carried out on a Quantum Design MPMS-5S SQUID magnetometer in the temperature range of 2–350 K at a magnetic field of 5000 Oe. The calorimetric measurements were performed on

Table 4. Crystallographic characteristics and the X-ray data collection and structure refinement statistics for complex **1*** at 240.0(2) and 293.0(2) K

Parameter	240.0(2) K	293.0(2) K
<i>a</i> /Å	10.6069(9)	10.601(2)
<i>b</i> /Å	30.644(3)	31.706(8)
<i>c</i> /Å	12.1996(13)	12.201(3)
β/deg	113.124(6)	114.515(14)
<i>V</i> /Å ³	3646.8(6)	3731.3(14)
<i>d</i> _{calc} /g cm ⁻³	1.238	1.210
μ/mm ⁻³	0.512	0.501
θ-Scan range/deg	2.19–28.13	2.21–28.68
Number of measured reflections	16054	17445
Number of independent reflections	4350	4795
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	1993	2227
<i>R</i> _{int}	0.0887	0.0849
Number of refined parameters	213	214
GOOF	0.872	0.824
<i>R</i> ₁ (<i>I</i> > 2σ _{<i>I</i>})	0.0420	0.0442
<i>wR</i> ₂	0.0817	0.0983
<i>R</i> ₁ (based on all data)	0.1202	0.1089
<i>wR</i> ₂	0.1026	0.1184

* The molecular formula C₄₀H₄₈CoN₂O₄, the molecular weight is 679.73, space group *C2/c*, *Z* = 4.

a DSC Phoenix 220 FI NETSCH differential scanning calorimeter.

Synthesis of complex 1. A mixture of warm solutions of Co(3,6-DBSQ)₃ (0.058 g, 0.081 mmol) and 1,10-phenanthroline (0.015 g, 0.083 mmol) in diethyl ether was kept for 1 day. The color of the solution changed from dark blue-green to dark olive. The dark crystals were separated by filtration and dried *in vacuo*. The yield was 0.040 g (73%). Found (%): C, 71.40; H, 6.87; N, 3.75; Co, 8.19. C₄₀H₄₈O₄N₂Co. Calculated (%): C, 70.67; H, 7.11; N, 4.14; Co, 8.67.

X-ray diffraction study. The single-crystal X-ray diffraction data sets were collected on a SMART APEX II CCD diffractometer (Bruker AXS) (Mo-K α radiation, $\lambda = 0.71073$ Å, absorption corrections were applied with the use of the Bruker SADABS software, version 2.10). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were positioned geometrically and refined using the riding model. The calculations and structure refinement were carried out with the use of the Bruker Shelxtl software, Version 6.14. The crystallographic characteristics and the X-ray data collection and structure refinement statistics for the complexes are given in Table 4.

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