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Redox Isomerism in *o*-Semiquinonato Cobalt Complexes in the Crystalline Phase

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Abstract—The key regularities of redox isomerism of six-coordinate bis-semiquinonato cobalt complexes in the crystalline phase are considered. The factors determining the temperature of transition between the redox isomers of various cobalt complexes (mononuclear and binuclear complexes, coordination polymers) were described. The transition parameters were shown to depend not only on the electronic and spatial structure of the ligands in a particular complex, but also on the crystal structure of the complex and intermolecular interactions in the lattice.

Keywords: redox active ligands, *o*-quinones, redox isomerism, cobalt
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INTRODUCTION

The term "redox isomerism" (or valence tautomerism) dates back to the early 1980s. It can be defined as a type of structural isomerism involving reversible intramolecular electron transfer between a transition metal ion and the redox active ligand present in the metal coordination sphere. This phenomenon is known for a broad range of complexes. An evident necessary condition is the presence, in the complex, of a transition metal ion capable of changing its oxidation state and one or several redox active ligand molecules. The transitions between redox isomers (valence tautomers) have been observed for complexes of vanadium [1], manganese [2–5], iron [6], cobalt [7, 8], nickel [9, 10], copper [11, 12], rhodium [13, 14], iridium [15], ruthenium [16], and ytterbium [17] with o-quinone, α-diimine, and o-aminophenol derivatives as redox active ligands. Initially, these transitions were found in solutions [11, 13, 18], but later it was shown that interconversion of redox isomers can also take place in the crystalline phase [19]. As a result, studies of these processes went beyond the framework of a purely fundamental problem, and redox isomers started to be considered as potential precursors of new materials for microelectronics, molecular switches, and memory devices.

The redox isomerism is addressed in numerous reviews [8, 20]. However, quite a number of publications of the authors' research group are not mentioned (or mentioned very rarely) in the listed reviews. These publications receive particular attention in the present review. We have chosen for consideration one of extensively studied classes of compounds exhibiting redox isomerism in the crystalline phase, namely, six-coordinate bis-*o*-semiquinonato cobalt complexes with N-donor ligands. In these compounds, the redox isomeric transition (Fig. 1) occurs between states with different charge distribution and spin multiplicity under the action of some external stimulus such as pressure, electromagnetic radiation, strong magnetic field and, first of all, temperature.

In the low-spin (or low-temperature) form, the low-spin Co(III) ion is bound to one *o*-semiquinonato and one catecholate ligands, while the high-spin (high-temperature) form is the bis-*o*-semiquinonato complex of the high-spin Co(II) ion. It should be emphasized that the reversible intramolecular electron transfer is accompanied, in this case, by a change in the cobalt spin multiplicity (spin-crossover), which is not typical for redox isomers of other transition metals, in particular, manganese.

Similarly to spin-crossover, transition between redox isomers is an entropy-driven process [20, 21]. The occupancy of redox states is determined by the Gibbs energy

$$\Delta G = \Delta G(\mathrm{Co}^{\mathrm{II\text{-}HS}}) - \Delta G(\mathrm{Co}^{\mathrm{III\text{-}LS}}) = \Delta H - T\Delta S.$$

The entropy increase ΔS upon transition between the isomers consists of the electronic component (ΔS_{el}) associated with the increase in the spin multiplicity of the complex and the vibrational component (ΔS_{vib}) associated with the change in the density of vibrational modes of the molecular skeleton as a result of bond elongation between the metal and the ligand. At low temperature, the entropic contribution is incommensurably small in comparison with the

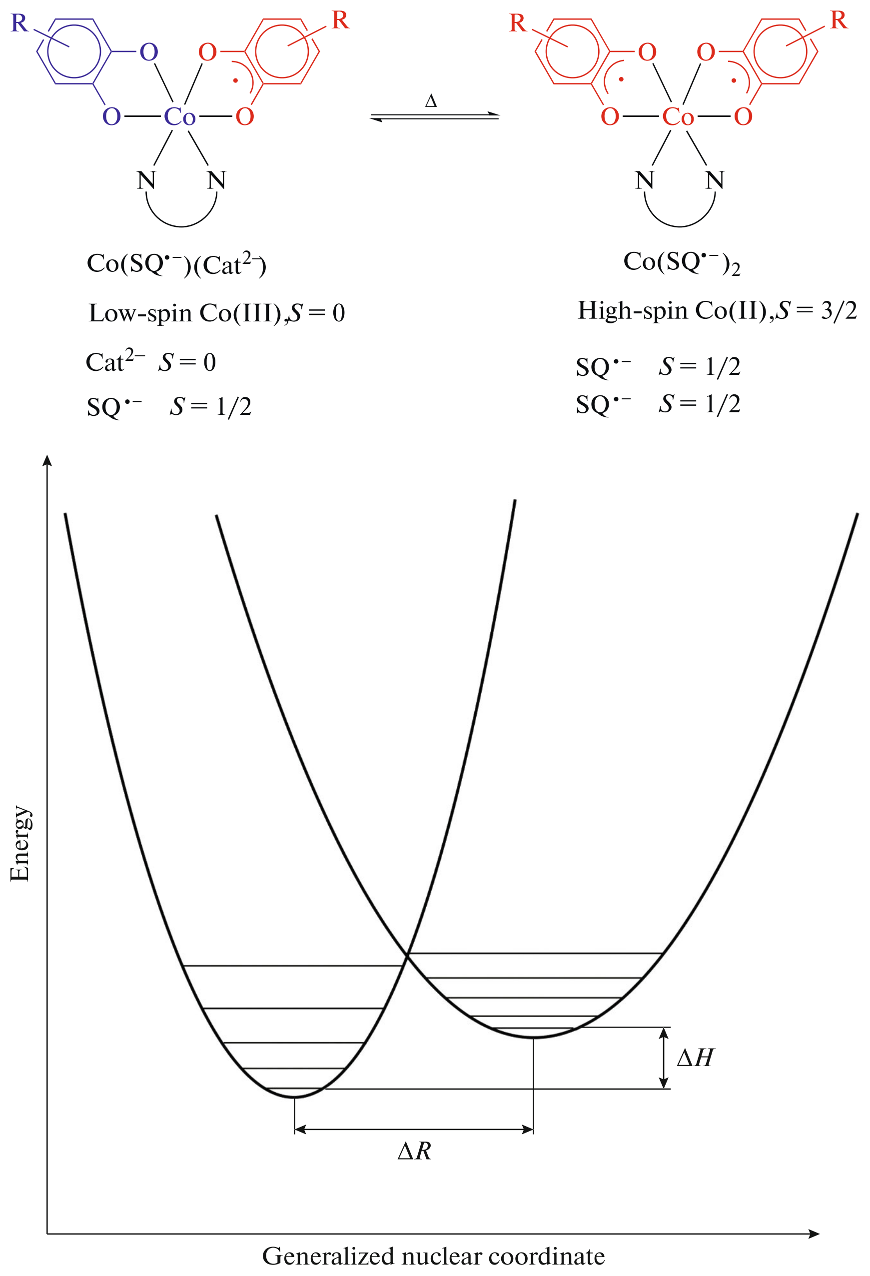

Fig. 1. Qualitative potential energy diagram of the states corresponding to redox isomers.

enthalpy change, with the more polar $\mathrm{Co^{III\text{-}LS}(SQ)(Cat)}$ form being the ground state (SQ and Cat = the mono- and direduced forms of *o*-quinone, respectively). On heating, the entropic contribution becomes commensurable with the ΔH value, and the high-spin state $\mathrm{Co^{II\text{-}HS}(SQ)_2}$ becomes more energetically favorable.

MONONUCLEAR COBALT COMPLEXES WITH BIDENTATE N-DONOR LIGANDS

The active research of the redox isomerism of *o*-semiquinonato transition metal complexes in the solid phase started in the 1990s [19, 22–24]. Historically, the complex (Bipy)Co(3,6-DBSQ)(3,6-DBCat) (**I**), where 3,6-DBSQ and 3,6-DBCat are singly and doubly reduced 3,6-di-*tert*-butyl-*o*-benzoquinone, Bipy is 2,2'-bipyridine, obtained by our research group is one of the first examples of bis-*o*-semiquinonato cobalt derivatives that exhibited a redox isomeric transition in the crystalline state [22]. The ESR spectrum of the polycrystalline sample of the complex at 120 K is typical for transition metal *o*-semiquinonato complexes where the unpaired electron is localized on the ligand. With temperature rise, the spectrum is broadened and at 260 K, it is no longer

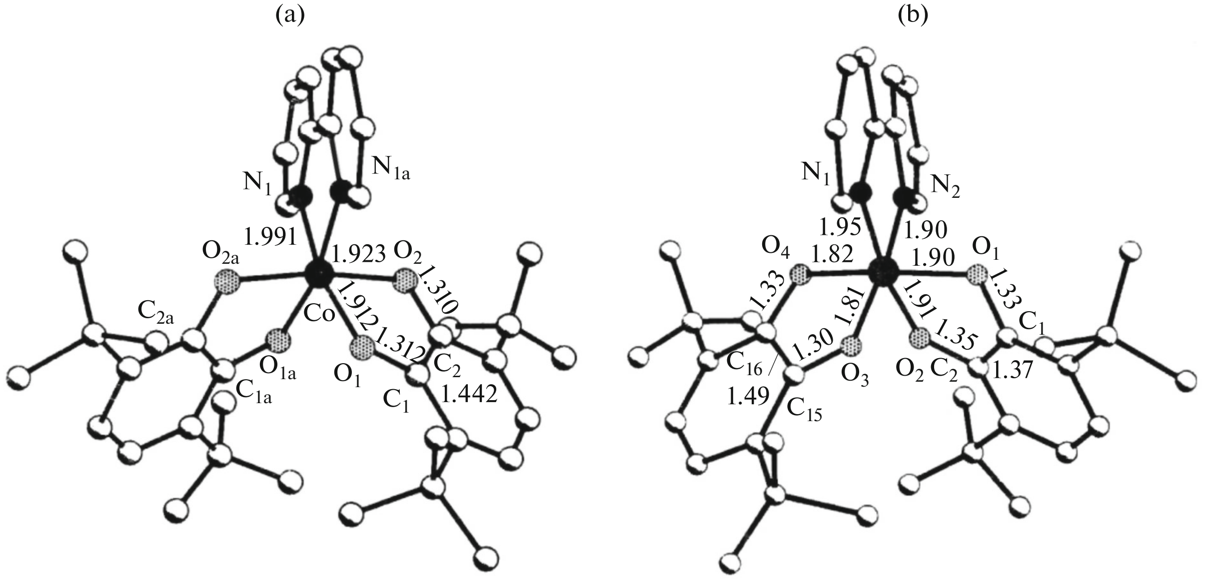

Fig. 2. Molecular structure and bond lengths in complex **I** at (a) 293 and (b) 153 K.

observable. The temperature dependence of the effective magnetic moment (μ_{eff}) is S-shaped. As the temperature decreases, μ_{eff} decreases from ~4.5 μ_B (420 K) to 2.1 μ_B (280 K), then smoothly declines to 1.95 μ_B, and remains virtually unchanged on further cooling down to 70 K. The high-temperature magnetic moment is close to the spin-only value (4.58 μ_B) corresponding to a system of one high-spin Co(II) ion (S = 3/2) and two *o*-semiquinonato ligands ($S = 1/2$). The low-temperature magnetic moment of complex **I** is close to the theoretical value for a species containing one unpaired electron (1.73 μ_B). Thus, the ESR and magnetochemical data evidence about the conversion of bis-*o*-semiquinonato Co(II) complex to the *o*-semiquinonato-catecholate Co(III) complex, in which the metal ion occurs in the low-spin state and is diamagnetic, and the single unpaired electron is localized on the *o*-semiquinonato ligand. The X-ray diffraction data for complex **I** at 153 and 293 K have been presented as evidence for redox isomeric transition (Fig. 2).

In both structures, the cobalt ion has a distorted octahedral geometry of the ligand environment. The reflection intensity statistics indicates that at room temperature, the structure of the complex is centrosymmetric, whereas at 153 K, a center of symmetry is absent. A comparison of the Co–O and Co–N bond lengths and the C–O and C–C bond lengths (in the *o*-quinone ligands) provides the conclusion that the structure established at 293 K corresponds to the bis-*o*-semiquinonato Co(II) complex, whereas the other structure corresponds to the *o*-semiquinonato-catecholate Co(III) derivative.

The complex was studied by differential scanning calorimetry (DSC). The temperature dependence of the heat capacity shows a noticeable deviation from the normal pattern at 260 K. This indicates that a phase transition takes place at this temperature, which, moreover, coincides with the temperature of the beginning of redox isomeric transition. Thus, in relation to complex **I** we have demonstrated for the first time that transition between the redox isomers in the crystalline phase is accompanied by a phase transition.

It was shown that varying the electron-acceptor ability of the *o*-quinone ligand in complexes of similar composition shifts the temperature range of the transition between redox isomers in the crystal. This is caused by the change in the energy gap between the π*-orbital of the ligand and the e_g-orbital of the metal fragment between which the electron transfer takes place [25, 26]. This is confirmed by magnetochemical measurements and precision calorimetry for three complexes of the type (Bipy)Co(DBSQ)(DBCat) containing 3,6-di-*tert*-butyl-*o*-benzoquinone (**I**), 4-me-thoxy-3,6-di-*tert*-butyl-*o*-benzoquinone (**II**), and 4-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone (**III**) as the redox active ligands [19, 27–30].

In the case of **II**, the presence of an electron-donor substituent in the *o*-quinone ligand stabilizes the bis-*o*-semiquinonato form of the complex, thus shifting the range of transition between redox isomers (with respect to that of **I**) towards lower temperature (Fig. 3). In complex **III**, the chloro-substituted *o*-quinone is a stronger acceptor than the 4-methoxy *o*-quinone in **II**; hence, the catecholate orbital is lower in energy, the energy gap is greater than that in **I**, and the transition temperature is higher (Fig. 4).

The properties of the N-donor ligand also have a considerable effect on the redox isomeric transition of

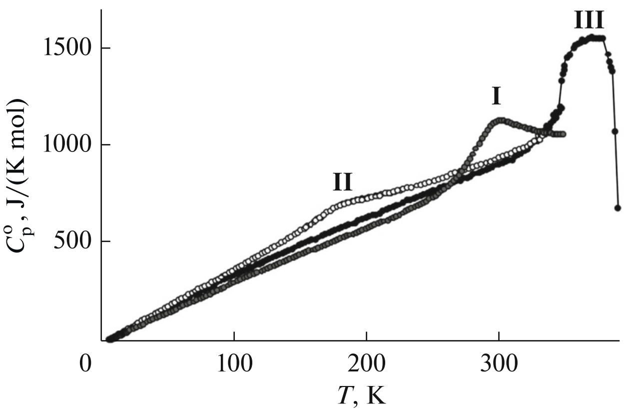

Fig. 3. Temperature dependences of heat capacity of complexes **I**–**III**.

the complex. A series of complexes (N-N)Co(3,5-$DBSQ)_2$, where N-N is a diimine ligand such as 4,4'-diphenyl-2,2'-bipyridine (Dpbipy), 4,4'-dimethyl-2,2'-bipyridine (Dmbipy), 2,2'-bipyridine (Bipy), 1,10-phenanthroline (Phen), 2,2'-dipyrimidine (Bipym), and 2,2'-bipyrazine (Bipyz), have been reported in [23, 24]. Considering the temperature dependences of the UV/Vis spectra, the authors demonstrated that all of the complexes show redox isomerism in solution, the transition temperature being determined by the N-donor nature and increasing in the series Bipyz > Bipym > Phen > Bipy > Dmbipy > Dpbipy. Meanwhile, in the crystalline state, the Dpbipy and Dmbipy complexes (and also the previously studied Bipy complex [31]) exist as *o*-semiquinonato-catecholate derivatives of the low-spin Co(III) ion, while their analogs containing Bipyz or Bipym are bis-*o*-semiquinonato complexes of the high-spin Co(II) ion; this was confirmed by X-ray diffraction and magnetic measurements. In the authors' opinion, the observed trends are attributable to different π-acceptor abilities of the N-donor ligands, which can be estimated from their first reduction potentials: Bipyz (–1.70 V) > Bipym (–1.80 V) > Phen (–2.04 V) > Bppy (–2.18 V) > Dmbipy (–2.40 V). The strong π-acceptors (Bipyz and Bipym) stabilize the $Co^{II}SQ_2$ form of the complex, whereas the weak π-acceptors (Bipy, Dmbipy) promote, conversely, the formation of the *o*-semiquinonato-catecholate complexes.

An important factor is also structural rigidity of the neutral ligand, which was confirmed for the series of complexes $Co(Me_2N(CH_2)_nNMe_2)(3,6\text{-}DBQ)_2$ (n = 1, 2, 3 for *N*,*N*,*N*',*N*'-tetramethylmethylenediamine (Tmda), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (Tmeda), *N*,*N*,*N*',*N*'-tetramethylpropylenediamine (Tmpda), respectively) [32]. According to X-ray diffraction data, the cobalt atoms in all three complexes have a distorted octahedral geometry of the ligand environment. Proceeding from the results of magnetochemical measurements, the authors estimated the transition temperatures between the redox isomers: $T_{1/2}$ > 350 (Tmda), ~310 (Tmeda), and 178 (Tmpda). The considerable decrease in the transition temperature for $(Tmpda)Co(3,6\text{-}DBQ)_2$ was attributed to the conformational flexibility of Tmpda, which makes a contribution to the entropy change upon the transition.

When Phen was used as the N-donor ligand, we obtained the complex $(Phen)Co(3,6\text{-}DBSQ)_2$ (**IV**) [33]. Since 1,10-phenanthroline is a stronger π-acceptor than 2,2'-bipyridine, the temperature range of transition between the redox isomers for this complex is shifted to lower temperature relative to that of **I**. In addition, according to magnetochemical measurements, the interconversion of redox isomers occurs within a narrower temperature range (250–350 K) than that in the previously described solvated derivatives $(Phen)Co(3,6\text{-}DBSQ)_2 \cdot C_6H_6$ [34]. The complex was characterized by X-ray diffraction at 240 and 293 K. Both structures were solved with space group *C*2/*c*; however, the Co–O and Co–N bond lengths are generally shorter at 240 K than at 293 K, which confirms the change in the cobalt atom charge or spin

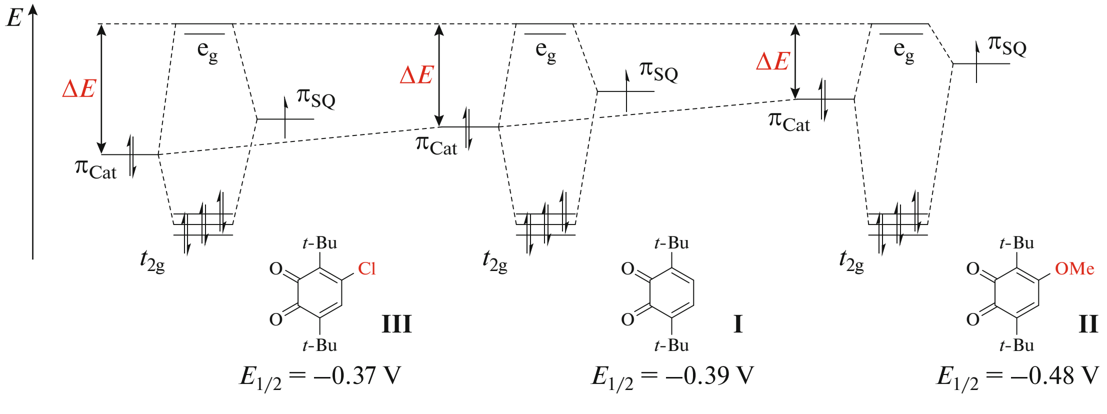

Fig. 4. Frontier orbitals diagram for complexes **I**–**III**.

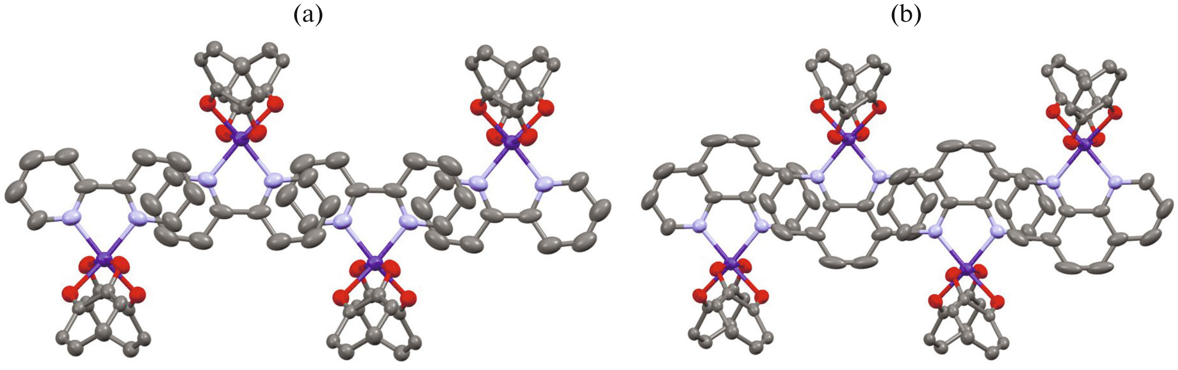

Fig. 5. Fragments of the crystal packing of complexes (a) **I** and (b) **IV**. View along the normal to the neutral ligand plane. The *tert*-butyl substituents are omitted.

multiplicity. The change in the C–O and C–C bond lengths in metallacycles also reflects a change in the effective charge on the *o*-quinone ligands. Thus, structural data confirm the transition between redox isomers of the complex.

Attention is attracted by the fact that isostructural complexes **I** and **IV**, which differ only by two carbon atoms in the neutral ligand (2,2'-Bipy and 1,10-Phen), have markedly different transition ranges (105 and 41 K for **I** and **IV**, respectively). The packing of both complexes is based on a 1D motif of neutral ligand planes (Fig. 5).

The pyridine moieties of both ligands are rotated relative to each other through 10.74° (2,2'-Bipy, 100 K) or 4.26° (1,10-Phen, 100 K). This difference is quite reasonable in view of the higher aromaticity of phenanthroline. With the overlap areas of these ligands in the stack being comparable, one can assume that more planar phenanthroline molecules would interact more strongly than the pyridine moieties of bipyridine, which are slightly rotated relative to each other. As a consequence, the transition occurs in a narrower temperature range, which reflects a higher degree of cooperativity.

Relatively recently [35], we obtained solid solutions of complexes **I** and **IV** with different component ratios (2 : 1, 1 : 1, 1 : 2, 1 : 4, 1 : 8, and 1 : 16). These complexes are isostructural and have similar crystal lattice parameters. The DSC, X-ray diffraction, and magnetochemistry data confirm that the samples were actually co-crystallized complexes rather than mixtures of crystals of two complexes. The temperatures and enthalpies of transitions between the redox isomers in solid solutions were determined from DSC data. The resulting values were represented as composition–property diagrams. The transition enthalpy was found to follow a linear dependence on the composition on going from one pure complex to another. However, the transition temperature–composition phase diagram was shaped as a convex arch. From this, one can conclude that superposition of the two lattices stabilizes the low-temperature *o*-semiquinonato-catecholate form (Fig. 6).

It is noteworthy that a complex with 5-nitro-1,10-phenanthroline (NO_2-Phen) similar to **IV** does not show redox isomerism in the crystalline phase [36]. Considering the temperature dependence of the UV/Vis spectra, the authors concluded that transition between redox isomers of the complex occurs in a toluene solution. However, in the crystalline state, it is a six-coordinate complex of the high-spin cobalt ion, and its electronic structure does not change with temperature. According to the authors' opinion, the inability of the complex to change its charge distribution is due to its trigonal-prismatic geometry and the related orbital energy distribution in the trigonal-prismatic ligand field. This type of geometry is inherent only to high-spin Co(II) compounds, whereas complexes with an octahedral ligand environment can exist in the $Co^{II}(SQ)_2$ and $Co^{III}(SQ)(Cat)$ states. Thus, the trigonal-prismatic geometry of the complex in the crystalline phase prevents the electron transfer between the metal and the *o*-semiquinonato ligand.

The complex with 2,9-dimethyl-1,10-phenanthroline $(2,9\text{-}Me_2\text{-}Phen)Co(3,6\text{-}DBSQ)_2$ (**V**), which we prepared, also exists in the bis-*o*-semiquinonato form over the whole temperature range, which is confirmed by magnetochemical measurements and X-ray diffraction [37]. The μ_{eff} values for compound **V** in the 50–300 K range are 4.12–4.30 μ_B, which is typical for bis-*o*-semiquinonato derivatives of the high-spin Co(II) ions [38]. According to our opinion, the fact that no redox isomerism is observed in this case can be explained by steric factors. It is known that upon transition to the low-temperature form, the Co–O and Co–N bond lengths are shortened; this change is 0.16–0.22 Å for various derivatives [39, 40]. In the case of complex **V**, the presence of methyl groups prevents a decrease in the volume of the coordination polyhedron, thus hampering transition of the complex to the low-temperature form.

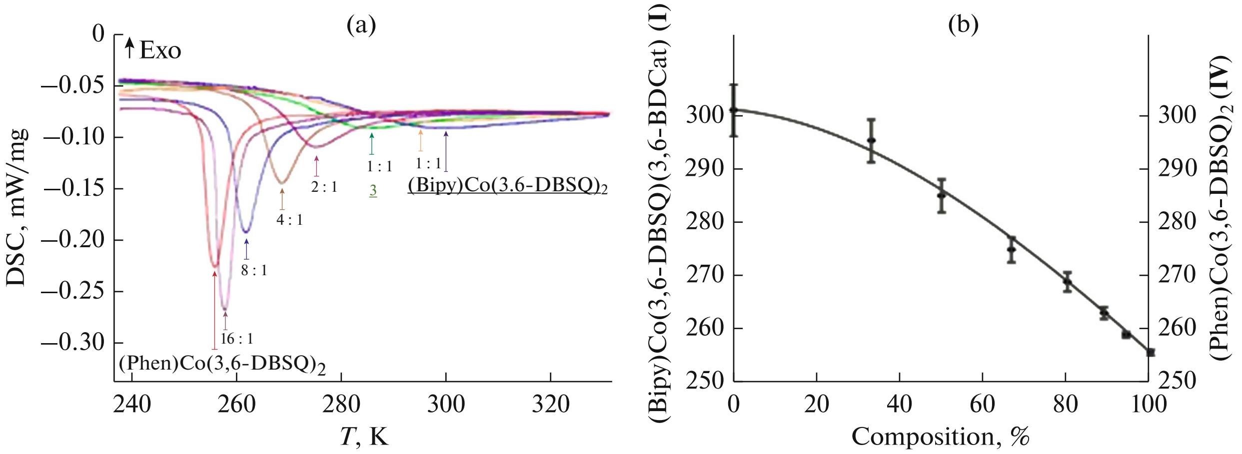

Fig. 6. (a) DSC curves and (b) transition temperature–composition diagram for solid solutions of complexes **I** and **IV** with different component ratios.

Unusual results were obtained in a study of redox isomerism of the complex (Phen)Co(4-OMe-3,6-DBSQ)$_2$ · $C_6H_5CH_3$ (**VI**) [37]. In view of the fact that the methoxy-substituted *o*-semiquinonato is a substantially weaker acceptor (4-OMe-3,6-DBQ, $E_{1/2}$ = –0.48 V vs. $E_{1/2}$ = –0.39 V for 3,6-DBQ), the transition of this compound should have been observed at temperatures much below 254 K (the transition temperature of complex **IV**). However, according to magnetochemical measurements and precision adiabatic calorimetry, the introduction of the methoxy group affects only the width of the transition range (240–281 and 237–316 K for **IV** and **VI**, respectively), but does not affect the transition temperature ($T_{1/2}$ = 254 K). We believe that this discrepancy is caused by the presence of solvent molecules in the lattice of complex **VI**—a similar effect was described by D. Hendrickson and co-workers for the above-mentioned complexes, (Phen)Co(3,5-DBSQ)$_2$ · C_6H_5Cl and (Phen)Co(3,5-DBSQ)$_2$ · $C_6H_5CH_3$ [24], and by C. Boscovic, who studied solvated samples of (Py)$_2$Co(3,5-DBSQ)$_2$ (Py = pyridine) [41].

In some cases, specific features of the crystal lattice and/or structure of the neutral ligand give rise to a kinetic barrier between the redox isomers and, as consequence, a hysteresis loop in the temperature dependence of the magnetic moment. This feature opens up prospects of using redox isomers as elements of memory devices. The temperature hysteresis of magnetization was observed by Hendrickson and co-workers [24] for the complex (Phen)Co(3,5-DBSQ)$_2$ · $C_6H_5CH_3$, it was amounted 5 K. However, the cited authors do not offer an explanation for the observed phenomenon. The origin of magnetization hysteresis has been considered in most detail in relation to (Py$_2$O)Co(3,6-DBQ)$_2$ [42]. This complex exists in two crystalline forms, differing by the crystal structure and magnetic properties. The sample of the complex isolated from toluene retains the charge distribution of Co^{II}(SQ)$_2$ over the whole temperature range studied (Fig. 7a). In the crystal lattice, the molecules form 1D stacks with π–π interactions between planar di(2-pyridyl) ether moieties.

Conversely, a sample of the same complex crystallized from acetone exists at room temperature as Co^{III}(Cat)(SQ). In this case, the bis(pyridyl) ether ligands are non-planar, with the dihedral angle between the pyridine planes being 36°. As a result of non-planarity of neutral ligands, molecules of the complex do not form 1D stacks. The effective magnetic moment of the complex slightly increases on heating in the 50–320 K range from ~1.8 to 1.9 μ_B. Further heating leads to a sharp jump of the magnetic moment associated with the Co^{III}(Cat)(SQ) → Co^{II}(SQ)$_2$ transition to reach 4.3 μ_B at 340 K (the transition temperature $T_{1/2}\uparrow$ = 330 K). On the subsequent cooling down to 120 K, the magnetic moment slightly decreases; then it sharply drops to 2.1 μ_B at 100 K (for the Co^{II}(SQ)$_2$ → Co^{III}(Cat)(SQ) transition, $T_{1/2}\downarrow$ = 100 K) (Fig. 7b). Thus, the temperature hysteresis is ~230 K. According to explanation of the authors, π–π interactions along the stacks in the crystal lattice of the sample obtained from toluene prevent the distortion of the planar bis(pyridyl) ether ligand, which is needed for transition to the mixed-valence form. On the other hand, the less rigid crystal packing of the complex in the sample isolated from acetone allows conversion of the ligand to a planar conformation; however, this requires additional energy expenditure.

We have obtained and studied the complex (Py$_2$NH)Co(3,6-DBSQ)(3,6-DBCat) (**VII**) containing a structural analog of di(2-pyridyl) ether, namely, di(2-pyridyl)amine [43]. The presence of a broad charge transfer band Cat → SQ in the near IR region (~5000 cm^{-1}) indicates that the *o*-quinone ligands

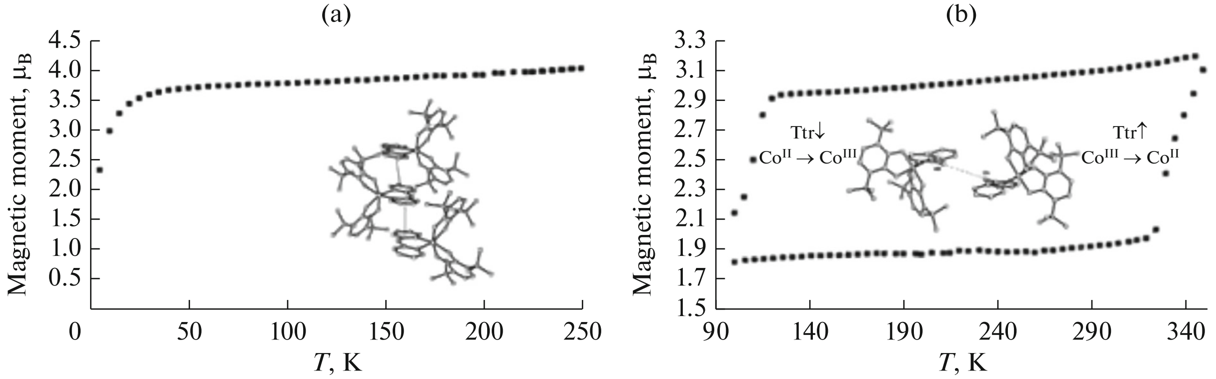

Fig. 7. Fragments of the crystal packing and temperature dependences of the magnetic moment for the samples of $(Py_2O)Co(3,6\text{-}DBSQ)_2$ obtained by crystallization from (a) toluene and (b) acetone.

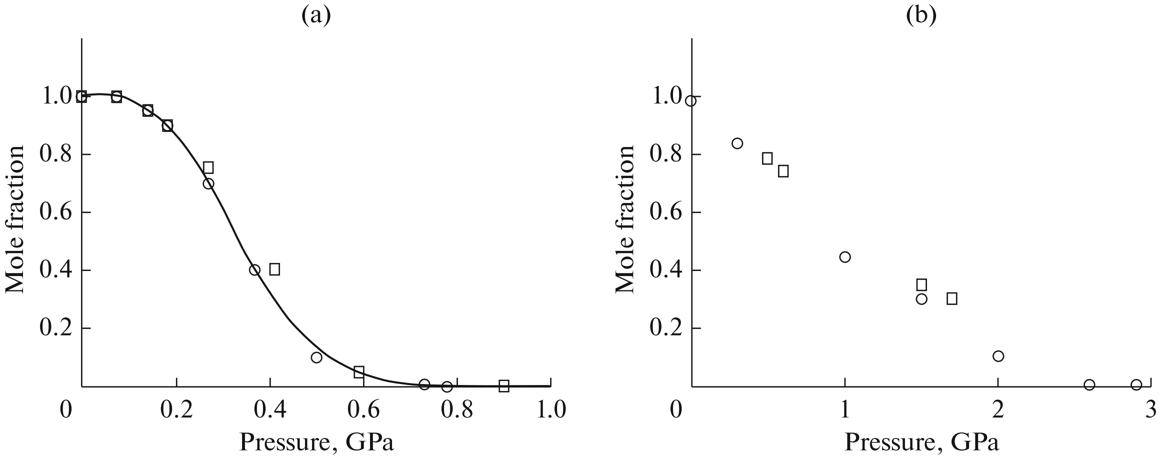

Fig. 8. Mole fraction of the $Co^{II}(SQ)_2$ form vs. pressure: (a) $(Phen)Co(3,5\text{-}DBSQ)_2 \cdot C_6H_5CH_3$, (b) non-solvated $(Phen)Co(3,5\text{-}DBSQ)_2$.

occur in this complex in different redox states. On heating in the 30–260 K range, μ_{eff} of the complex gradually grows from 2.1 to 2.4 μ_B. The presented values are slightly higher than the theoretical value for a system containing one unpaired electron localized on the *o*-semiquinonato ligand, which corresponds to the low-temperature form of the complex (1.73 μ_B). On further heating, the magnetic moment sharply grows as a result of redox isomeric transition. At 325 K, the μ_{eff} value is 2.72 μ_B, which indicates that the transition is not complete at this temperature. The results of magnetochemical measurements are confirmed by ESR data and precision adiabatic calorimetry.

All of the above-mentioned studies describe the thermally induced transitions between redox isomers. However, as noted above, the transitions of redox isomers of *o*-semiquinonato cobalt complexes can be induced by not only temperature, but also pressure [44], magnetic field [45], electromagnetic radiation [46], and soft [47] and hard [48] X-ray radiation.

In [44], the complex $(Phen)Co(3,5\text{-}DBSQ)_2$ and its toluene solvate have been studied by X-ray absorption spectroscopy (EXAFS and XANES). The interatomic distances in the inner coordination sphere of the metal in $(Phen)Co(3,5\text{-}DBSQ)_2 \cdot C_6H_5CH_3$ determined from the EXAFS data are in good agreement with the X-ray diffraction data obtained previously [24]. In addition, the authors studied the dependence of the mole fraction of $Co^{II}(SQ)_2$ for both complexes on the external pressure at room temperature using XANES (Fig. 8).

As noted above, the non-solvated $(Phen)Co(3,5\text{-}DBSQ)_2$ complex does not show a thermally induced redox isomeric transition [24] and exists as the bis-*o*-semiquinonato compound over the whole temperature range. However, the action of high pressure (2.5 GPa) induces complete transition to the mixed-valence form.

Using complex **I** as an example, we showed that the transition between redox isomers can be induced by an

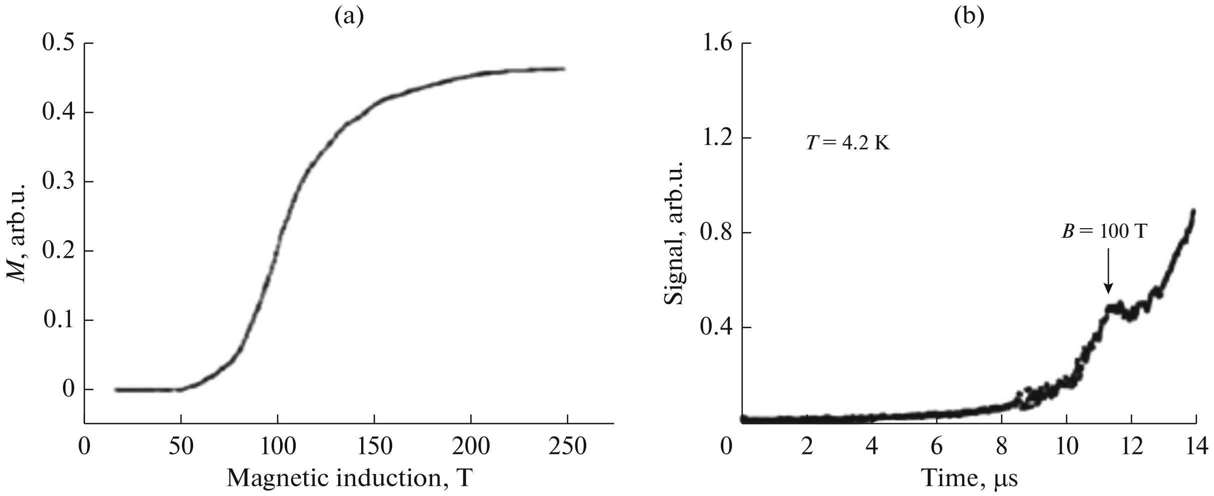

Fig. 9. (a) Magnetization of complex **I** vs. external magnetic field and (b) experimental time dependence of differential magnetization.

external magnetic field [45]. The increase of the magnetic field with time at 4.2 K results in an upsurge of the differential magnetization of the complex at a 100 T field.

On the basis of these results, we derived the dependence of the relative magnetization (M) for complex **I**, which correlates with the mole fraction of the high-spin form, on the external magnetic field induction (Fig. 9). This was used to calculate the entropy changes upon the transition between the redox isomers (ΔS = 7.45 J/mol K) and the energy difference between the isomers (ΔE = 2.23 kJ/mol).

Over the last 15 years, O. Sato's research group published several papers devoted to the regularities of the photoinduced redox isomerism in the *o*-semiquinonato cobalt complexes [46, 49–51]. The essence of the phenomenon is that the light irradiation of samples of the complexes at low temperature (2–80 K) at the 500–600 nm wavelength corresponding to the ligand-to-metal charge transfer (LMCT) induces transition of the complex from the $\text{Co}^{\text{III}}(\text{SQ})(\text{Cat})$ ground state to a metastable state characterized by a higher magnetic moment (Fig. 10).

On the basis of X-ray absorption spectroscopy [46], magnetochemical measurements, UV/Vis spectroscopy [49], and ESR spectroscopy [50], the authors interpret this metastable state as the high-temperature $\text{Co}^{\text{II- HS}}(\text{SQ})_2$ form, which is obtained upon thermal treatment. According to [53], exposure to light at the LMCT wavelength stimulates the electron transfer to give an intermediate short-lived $\text{Co}^{\text{II-LS}}(\text{SQ})_2$ state, from which the system rapidly relaxes to the metastable $\text{Co}^{\text{II-HS}}(\text{SQ})_2$ form. The subsequent slow relaxation of the system from the metastable state to the ground state occurs on temperature rise or can be induced by light at the metal-to-ligand charge transfer wavelength (~800 nm) [51, 52]. It should be noted that exposure to light does not induce complete transition to the metastable state, in the same way as photorelaxation does not bring the system completely back to the ground state. The authors [53] attributed this to the partial overlap of the ligand-to-metal charge transfer band of the ground state with the metal-to-ligand charge transfer band of the metsastable state. One more explanation is based on the fact that bulky crystalline samples are not completely transparent; therefore, the number of metastable molecules is greater on the crystal surface than in the bulk [46]. It is worth noting that the photoinduced redox isomerism is of interest as regards the prospects of application of these complexes as molecular electronics elements.

A new prospective practical use of the redox isomeric cobalt complexes was discovered relatively recently. Together with employees of the Institute for Physics of Microstructures, Russian Academy of Sciences (Nizhny Novgorod), we measured the temperature dependence of the conductivity of single-crystalline samples of complexes **I** and **IV** and amorphous and polycrystalline films of these complexes (obtained by vacuum sublimation) [54]. It was found that in the temperature range in which the redox isomeric transition takes place, this dependence has a pronounced maximum, after which the conductivity decreases to zero. The relative decrease in the conductivity reaches 10% per degree. The observed phenomenon allows considering these complexes as promising materials for highly sensitive uncooled bolometer arrays.

MONONUCLEAR COBALT COMPLEXES WITH MONODENTATE N-DONOR LIGANDS

Bis-*o*-quinone cobalt derivatives containing monodentate N-donor ligands can be considered as a

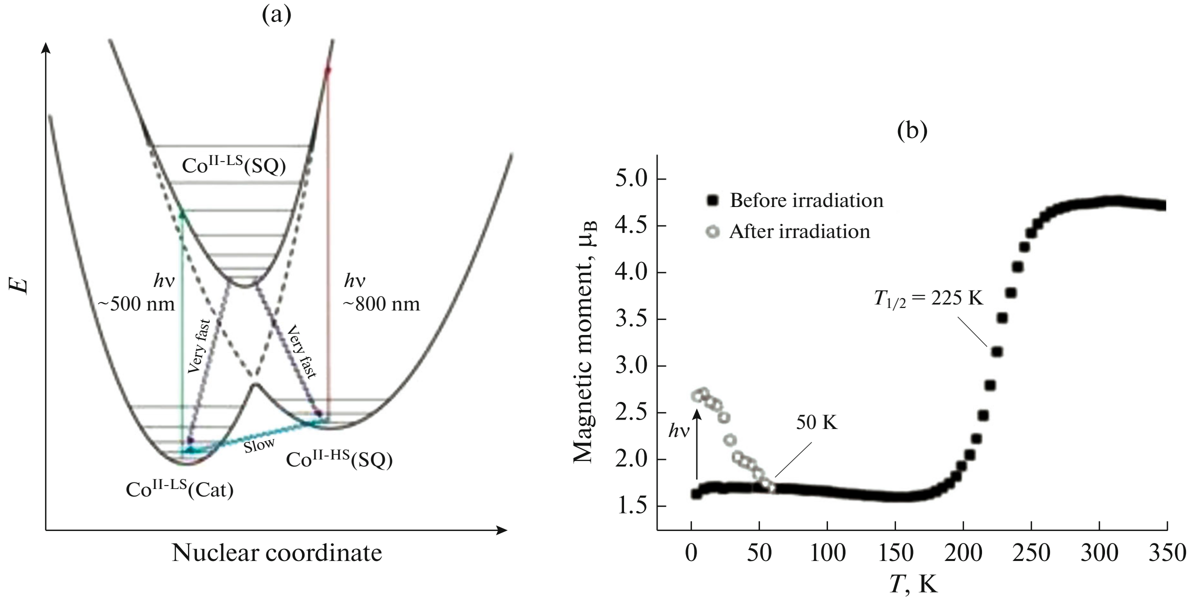

Fig. 10. (a) Qualitative potential energy diagram for the photoinduced redox isomeric transition and (b) temperature dependences of the magnetic moment for (Phen)Co(3,5-DBSQ)(3,5-DBCat) · C_6H_5Cl: (■) before and (○) after irradiation at λ = 532 nm.

separate class of redox isomers [55–58]. In these complexes, N-donor ligands are located, most often, in the *trans*-position, which prevents stacking via π–π-interaction between neutral ligands of the neighboring complex molecules.

The redox isomerism of complexes containing a variety of *para*-substituted pyridine derivatives as neutral N-donor ligands has been reported in [55, 56]. According to X-ray diffraction data, the cobalt atoms of all complexes are characterized by a distorted octahedral geometry, the neutral ligands are located in apical positions. On the basis of magnetic susceptibility data, the authors have shown that in the 10–300 K range, complexes with pyridines containing donor substituents (–CH_3, –OCH_3) are *o*-semiquinonato-catecholate derivatives of low-spin Co(III). The complexes with 4-cyanopyridine, 4-bromopyridine, and 4-nitropyridine exhibit a thermally and photo induced redox isomeric transition. All three compounds show hysteresis (5 K) in the magnetic susceptibility curve. An interesting fact is that the magnetic properties of the 4-cyanopyridine complex depend substantially on the rate of temperature change. The low-temperature magnetic susceptibility value corresponds to a species containing one unpaired electron. Gradual heating of a sample of the complex results in a sharp growth of the magnetic susceptibility in the 100–120 K range up to a value corresponding to the bis-*o*-semiquinonato form of the complex. On the subsequent slow cooling, the same curve of the temperature dependence is reproduced. However, the low-temperature value of the magnetic moment of the sample subjected to fast cooling corresponds to the charge distribution of $Co^{II}(SQ)_2$. The subsequent gradual heating leads to a sharp decrease in the magnetic susceptibility in the 80–100 K range. During the next temperature rise, the magnetic moment of the system varies similarly to the "slow cooling–slow heating" cycle. The authors attributed the observed thermal behavior of the complex to hydrogen bonding between the cyano groups and the hydrogen atoms in neighboring pyridine molecules and *o*-semiquinonato moieties. In addition, according to the authors' opinion, these interactions are one of the reasons for the transitions between redox isomers for the complexes $(PyX)_2Co$(3,5-DBCat)(3,5-DBSQ) (X = CN, Br, NO_2), as opposed to the 4-methylpyridine- and 4-methoxypyridine-containing derivatives, in the crystal lattices of which the hydrogen bonds are weak if at all present.

Researchers of the International Tomography Center, Siberian Branch of the RAS (Novosibirsk), together with our research group prepared the heterospin complexes $(NIT)_2Co(3,6\text{-}DBSQ)_2$ (**VIII**) and $(IN)_2Co(3,6\text{-}DBSQ)_2$ (**IX**) (NIT = 4,4,5,5-tetra-methyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide, IN = 4,4,5,5-tetra-methyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl) containing N-donor ligands functionalized with free radical groups [59]. The complexes were isolated and characterized as dichloromethane, acetone, and acetonitrile solvates. The data of magnetic susceptibility measurements indicate that, irrespective of the nature of the solvent molecules incorporated in the crystal lattice, all compounds undergo redox isomeric transition at temperatures above 250 K. The low-temperature μ_{eff} value for acetonitrile solvates is ~3.0 μ_B, which corresponds to a system of three non-

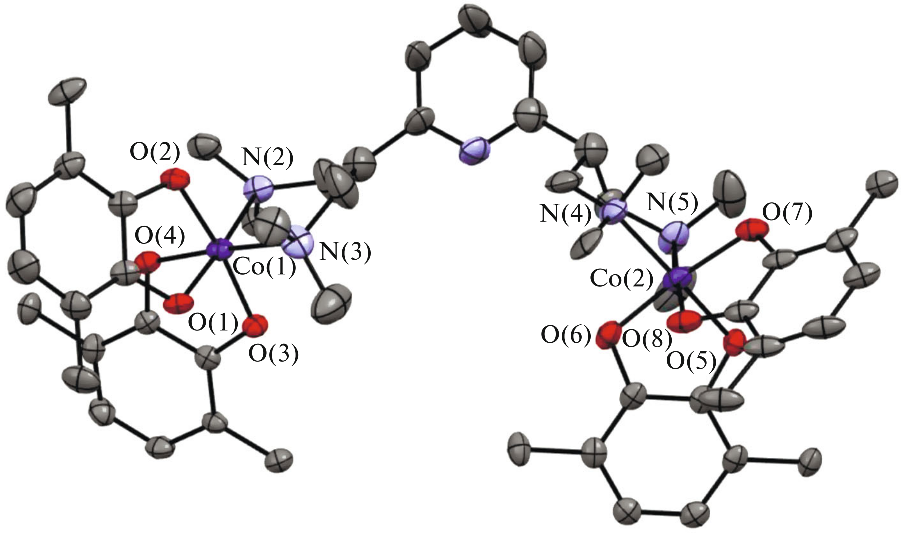

Fig. 11. Molecular structure of complex **X** (at 100 K).

interacting unpaired electrons (one *o*-semiquinonato and two nitroxide ligands). As the samples are heated to 350 K, the magnetic moment curve does not reach a plateau corresponding to the high-spin form of the complex; however, the magnetic moments at this temperature are substantially higher than the theoretical value for a system of high-spin Co(II) ion, two *o*-semiquinonato ligands, and two nitroxide radicals. This can be related to the spin–orbit coupling typical for the high-spin cobalt(II) ion in octahedral coordination environment.

BINUCLEAR COBALT COMPLEXES WITH BRIDGING N-DONOR LIGANDS

Several publications of the last 10 years are devoted to binuclear bis-*o*-quinone complexes exhibiting redox isomerism [60–62]. In these compounds, bis-bidentate N-donor ligands act as bridges between the metal centers. Along this line of research, we synthesized a series of complexes $(PyN_4)[Co(DBSQ)_2]_2$ (PyN_4 = 2,6-bis-(tetramethyl-1,3-diaminoisopropyl)pyridine, DBSQ = monoreduced forms of 3,6-di-*tert*-butyl-*o*-benzoquinone (**X**), 4,5-*N*,*N*'-piperazino-3,6-di-*tert*-butyl-*o*-benzoquinone (**XI**), and 4-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone (**XII**)) [63]. Complex **X** was characterized by X-ray diffraction at 100 and 250 K. The cobalt ions in both structures occur in a distorted octahedral environment (Fig. 11). Comparison of the bond lengths in the obtained structures with published data provides the conclusion that these structures correspond to two redox isomers of the complex at both metal centers.

The transition between redox isomers for all three derivatives was confirmed by ESR data and magnetochemical measurements. An unexpected fact is that the transition in all three complexes takes place at the same temperature (~200 K), while the transition temperature range increases in the series **X** < **XI** < **XII**. The same trend is also observed for the phase transitions detected by precision adiabatic calorimetry. In other words, for the presented binuclear complexes, the variation of the electron-acceptor properties of *o*-quinone ligands does not induce a change in the temperature of redox isomeric transition. This can be due to the nonrigid crystal packing, as indicated by the strong disorder of some molecular moieties.

COORDINATION POLYMERS

The use of N-donor ligands in which the nitrogen atoms are arranged in such a way that they cannot be coordinated to one metal center gives rise to coordination polymers. Historically, the complex $[(Pyz)Co(3,6\text{-}DBSQ)_2]_n$ (Pyz = pyrazine) was the first compound of this type exhibiting an intramolecular electron transfer between the metal and the *o*-quinone ligand [64]. According to X-ray diffraction data, this complex is a 1D coordination polymer in which the pyrazine molecules connect the square planar $Co(3,6\text{-}DBSQ)_2$ moieties. The μ_{eff} value of the complex at 350 K is 5.86 μ_B, which is much higher than the calculated value for species with the $Co^{II}(SQ)_2$ charge distribution (4.58 μ_B). The authors do not give any interpretation for the high μ_{eff} value. On cooling, the magnetic moment decreases and at 5 K, it reaches the value of 1.71 μ_B corresponding to a species with one unpaired electron. The magnetochemical data are in accordance with the spectral data for this complex in the crystalline phase.

One more polymeric complex was reported in [65]. In this case, the metal atoms are linked by 4,4'-bipyridine. The structure of this complex is similar to that of the pyrazine derivative described above. The complex exhibits a redox isomeric process over a relatively narrow temperature range of 300–350 K.

In conclusion, we would like to note that parameters of the redox isomeric transition of bis-*o*-semiquinonato cobalt complexes in the crystalline phase are determined, first of all, by the electron-acceptor properties of the *o*-quinone ligand and by σ-donor and π-acceptor properties, conformational rigidity, and steric bulkiness of the N-donor ligand. However, apart from the indicated molecular factors, the crystal structure and packing (including the solvate molecules) are also significant, which may in some cases give rise to a hysteresis loop in the temperature dependence of the magnetic moment of the complex.

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