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Heterospin complexes based on cobalt semiquinolate with nitroxides*

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Heterospin complexes based on cobalt semiquinolate with stable nitroxides of composition $[Co(SQ)_2(NIT)_2] \cdot 8CH_2Cl_2$, $[Co(SQ)_2(NIT)_2] \cdot 4MeCN$, $[Co(SQ)_2(IN)_2] \cdot 5Me_2CO$, $[Co(SQ)_2(IN)_2] \cdot 4MeCN$, and $[Co(SQ)_2(IN)_2] \cdot 2CH_2Cl_2 \cdot C_6H_{14}$, where SQ is 3,6-di-*tert*-butyl-*o*-benzosemiquinolate, NIT is 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl, and IN is the imine analog of NIT, *viz*., 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl, were synthesized. The characteristic feature of these compounds is that they contain two different types of paramagnetic organic ligands. The X-ray diffraction study showed that the solid phases of the complexes have a molecular structure. According to the data from thermomagnetic analysis (2—350 K), all complexes exhibit effects of valence tautomerism at ~20 °C. It was found that incorporated solvent molecules have an effect on the magnetic anomaly temperature.

Key words: cobalt, semiquinolates, nitroxides, X-ray diffraction analysis, valence tautomerism, magnetochemistry.

The design of new types of magnetically active compounds requires the development of methods for the directed construction of highly efficient exchange-coupled multispin ensembles.[1—15] One of approaches to the synthesis of such ensembles is based on the use of heterospin compounds, *viz*., transition metal complexes with organic radicals,[15—32] whose molecules contain paramagnetic centers of different nature with unpaired d (or f) and p electrons. Metal complexes with nitroxides[15—33] and *o*-semiquinone (*o*-iminosemiquionone) metal complexes[34—37] comprise the most representative classes of such compounds. Many complexes belonging to these classes can be magnetized in the solid state.[15,16,18—20,25,28—32] Known synthetic approaches provide a way to prepare magnetically active compounds containing simultaneously a stable organic radical and two or more paramagnetic metal centers.[28,31—33,38]

Both antiferro- and ferromagnetic exchange interactions can occur between the magnetic centers in heterospin transition metal complexes with *o*-semiquinolate ligands. The geometry of the complexes is one of the factors that influence the character of these interactions, and the magnetic properties of the complexes can be controlled by varying the geometric parameters. The addition of neutral ligands to square-planar low-spin bis-*o*-semiquinone Ni^{II} complexes affords high-spin five- or six-coordinate complexes.[39—41] Recently, it has been shown[41] that the reaction of copper(II) bis(3,6-di-*tert*-butyl-*o*-benzosemiquinolate) $[Cu(SQ)_2]$ with neutral aza ligands is accompanied by the transformation of the geometry resulting in a considerable change in the ratio of the ferro- to antiferromagnetic exchange in the $[Cu(SQ)_2]$ matrix. In the cited study, the first heterospin Cu^{II} complex with paramagnetic ligands of different nature, *viz*., the *o*-semiquinone radical anion and stable 2-imidazoline nitroxide, was isolated and characterized.[41] In continuation of these investigations, we synthesized first heterospin complexes based on cobalt *o*-semiquinolate with nitroxides, *viz*., 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (NIT) and its imine analog, 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (IN). The structures and thermomagnetic properties of these complexes were investigated.

Results and Discussion

Transition metal complexes with *o*-semiquinolate ligands characterized by valence tautomerism[34—36,43—50]

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* Dedicated to Academician V. N. Charushin on the occasion of his 60th birthday.

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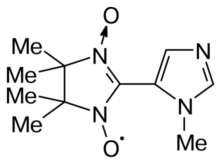
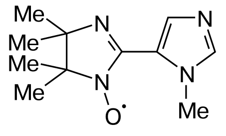
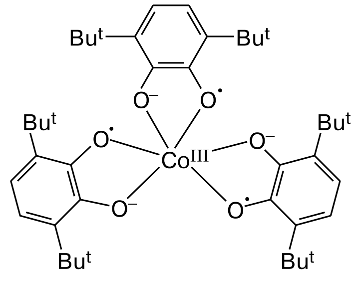


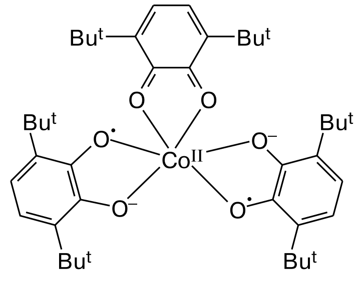
NIT



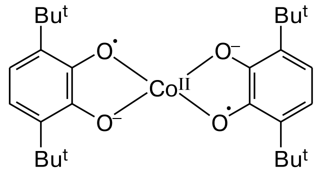
IN



Co(SQ)$_3$



Co(SQ)$_2$Q



Co(SQ)$_2$

are valuable compounds for molecular spintronics.[51—54] Systematic studies of specific thermally and photoinduced magnetic effects typical of this class of compounds show promise for the use of these compounds in the design of components of sensors and switches sensitive to external effects.[54—66] In some cases, thread-like crystals of these complexes exhibit the photo/thermomechanical effect.[44,65,67,68] Mixed-ligand complexes based on Co^{II,III} semiquinolate with nitrogen-containing heterocycles are being extensively studied in this respect. This stimulated us, first, to investigate the possibility of the synthesis of mixed-ligand complexes based on cobalt *o*-semiquinolate and nitroxides and, second, to reveal the possibility of the existence of valence tautomerism for these multispin compounds and to find the temperature range, where this effect is manifested. We used NIT and its imine analog IN containing the heterocyclic N donor atom in the side chain as nitroxides.

Synthesis of solvates and their properties

It is known that three radical anions in the complex [Co(SQ)$_3$] are coordinated to the metal ion in the low-spin state. The radical-anion ligands are linked to each other by an antiferromagnetic exchange interaction. At low temperature, the magnetic moment corresponds to one unpaired electron (S = 1/2); the high-temperature value of the effective magnetic moment of [Co(SQ)$_3$] is close to the value for three unpaired electrons. In solution, the complex Co(3,6-DBSQ)$_3$ is easily involved in the replacement reactions giving the bis(semiquinolate) complexes [Co(SQ)$_2$(η^1-L)$_2$] and [Co(SQ)$_2$(η^2-L)]. We synthesized a series of mixed-ligand solvates with the use of nitroxides NIT and IN as L: [Co(SQ)$_2$(NIT)$_2$] • 8CH$_2$Cl$_2$ (**1**), [Co(SQ)$_2$(NIT)$_2$] • 4MeCN (**2**), [Co(SQ)$_2$(IN)$_2$] • 5Me$_2$CO (**3**), [Co(SQ)$_2$(IN)$_2$] • 4MeCN (**4**), and [Co(SQ)$_2$(IN)$_2$] • 2CH$_2$Cl$_2$ • C$_6$H$_{14}$ (**5**). Particular attention was given to the development of methods for the isolation of these solvates as crystals suitable for X-ray diffraction. We failed to find solvents and conditions for crystallization of the complexes such that would allow us to obtain crystals, in which the solvent molecules are not included in the solid phase.

Crystals of **1**—**5** formed after storage of the mother liquors at temperatures below –10 °C. Hence, the crystals were generally grown in a cold chamber at –18 °C. To perform X-ray diffraction studies, a portion of crystals together with the mother liquor was taken out from the solution with a pipette and mixed with precooled epoxy resin on a glass slide coverslip. Single crystals of the solvates coated with a resin layer were mounted on a holder and transferred as rapidly as possible to the working area of the X-ray diffractometer, where the temperature was maintained at 240 K with a stream of nitrogen gas. At this temperature, single-crystal X-ray diffraction data sets for **2**—**4** were collected (Table 1). For solvate **4**, X-ray diffraction data were measured also at 115 K. No differences in the structure of complex **4** were found, and only the R factor for the X-ray diffraction data collected at 115 K was somewhat lower than that for the data collected at 240 K. Single crystals of compounds **1** and **5** containing CH$_2$Cl$_2$ molecules quite rapidly decomposed, and attempts to retard their degradation failed. For these compounds, the X-ray diffraction data sets were collected as rapidly as possible. Nevertheless, the R factors for complexes **1** and **5** containing labile CH$_2$Cl$_2$ molecules were high (see Table 1). However, these data were sufficient for the reliable determination of the molecular structures of the coordination compounds [Co(SQ)$_2$(NIT)$_2$] and [Co(SQ)$_2$(IN)$_2$] in the crystals of solvates **1** and **5**, respectively. The X-ray dif-

Table 1. Crystallographic characteristics for the complexes **1**—**5**

Parameter	**1**	**2**	**3**	**4**[a]	**4**[b]	**5**
Molecular weight	1653.51	1138.32	1232.49	1106.32	1106.32	1198.13
T/K	293(2)	240(2)	240(2)	115(2)	240(2)	298(2)
a/Å	11.542(3)	11.667(4)	12.0384(8)	11.349(4)	11.507(3)	10.442(9)
b/Å	12.868(3)	12.234(4)	14.5265(9)	12.057(4)	12.238(3)	11.857(9)
c/Å	14.380(4)	13.108(4)	22.7351(14)	13.380(4)	13.435(3)	14.408(12)
α/deg	97.253(6)	110.422(6)	72.537(5)	107.830(4)	109.541(3)	71.591(19)
β/deg	104.411(6)	103.464(6)	87.529(5)	104.496(4)	103.246(3)	84.656(19)
γ/deg	99.758(6)	106.014(6)	71.720(5)	108.005(4)	107.538(3)	72.490(17)
V/Å^3	2006.6(9)	1568.9(9)	3595.5(4)	1532.5(8)	1581.4(6)	1614(2)
d_{calc}/g cm^{-3}	1.368	1.205	1.138	1.199	1.162	1.233
μ/mm^{-1}	0.797	0.333	0.297	0.337	0.337	0.483
θ-Scan range/deg	2.00—26.48	1.78—26.42	2.45—28.37	1.73—26.54	1.94—26.49	2.46—23.47
I_{hkl}, measured/ independent	20247/8188	15864/6384	50751/17745	14660/6172	12984/6433	12565/4688
R_{int}	0.1127	0.1397	0.2739	0.0448	0.0378	0.3990
Number of refined parameters	468	368	767	349	349	350
GOOF	1.000	0.956	0.775	1.066	1.025	0.957
R_1	0.0926	0.0778	0.0688	0.0575	0.0628	0.1614
wR_2 ($I > 2\sigma(I)$)	0.2106	0.1345	0.1417	0.1448	0.1565	0.2410
R_1	0.1595	0.1359	0.3388	0.0714	0.0783	0.3033
wR_2 (based on all data)	0.2403	0.1579	0.2140	0.1596	0.1691	0.3193

[a] At 115 K.

[b] At 240 K.

fraction data allowed us to estimate the number of solvent molecules included in the solid phases.

Crystals of **1**—**5** together with the mother liquor were taken out from the cold chamber and filtered off as rapidly as possible; the operation took at most 10—20 s. This was because an increase in the temperature of the mother liquor leads to a sharp increase in the solubility of compounds **1**—**5**. Thus, the crystals completely dissolved within a few minutes after taking the reaction mixture from the cold chamber and keeping at ~20 °C. For this reason, the filtered crystals were washed very rapidly (within a few seconds) on a cold filter with a small portion of a precooled appropriate solvent. The crystals of the solvates separated from the mother liquor began to spontaneously lose incorporated solvent molecules and decompose. For the solvates with CH_2Cl_2 and Me_2CO, this process occurs much faster than for the solvates with MeCN. Because of this, after the separation from the mother liquor, washing, and rapid drying on a filter with an air flow, the crystals were rapidly transferred into a quartz tube and placed in the working area of a SQUID magnetometer (5 K) to perform magnetochemical measurements.

The X-ray diffraction studies of solvates **1**—**5** showed that their solid phases have a molecular structure. Figure 1 presents the molecular structures of the coordination compounds $[Co(SQ)_2(NIT)_2]$ and $[Co(SQ)_2(IN)_2]$ determined for solvates **1** and **5**, respectively. In complexes **1**—**5**, the Co atoms are in a centrosymmetric or pseudocentrosymmetric distorted octahedral environment. In the coordination units CoO_4N_2, the equatorial Co—O_{SQ} distances and the axial Co—N distances are in the ranges of 1.864(4)—1.883(3) and 1.910(4)—1.924(4) Å, respectively. In the SQ ligands, the C—O bond lengths (1.280(7)—1.328(6) Å) correspond to the values intermediate between the double bond lengths (1.22(1) Å in benzoquinone) and the single bond lengths (1.36(1) Å in phenol).[34,40—42] The N—O distances in the nitroxides have

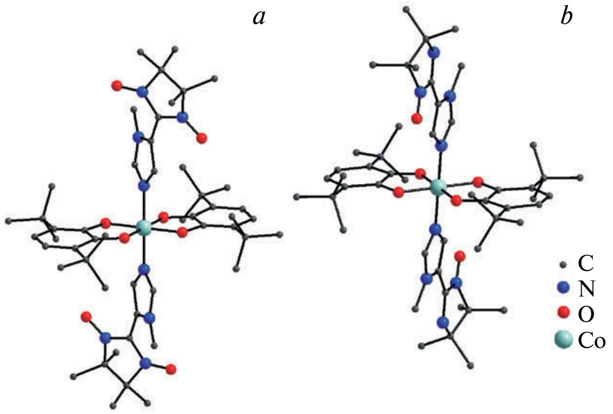


Fig. 1. Molecular structures of the complexes in solvates **1** (*a*) and **5** (*b*).*

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* Figs 1 and 2 are available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

typical values (1.265(4)—1.283(6) Å). Let us also note the characteristic feature of the pseudocentrosymmetric molecule $[Co(SQ)_2(IN)_2]$ in the crystals of **3**. In this molecule, the SQ ligands are non-equivalent: the differences in the Co—O and C—O bond lengths and the chelate O—Co—O angles are 0.05 Å, 0.05 Å, and 3.9°, respectively.

The crystals are characterized by the same molecular packing motif both for the complexes with NIT and IN (Fig. 2, *a*, *b*). As can be seen from Fig. 2, the coordination species $[Co(SQ)_2(NIT)_2]$ and $[Co(SQ)_2(IN)_2]$ in the solid phases are distant from each other because they are separated by a considerable number of solvent molecules included in the crystals. As a result, intermolecular exchange interactions between unpaired electrons of the paramagnetic centers in solid complexes **1**—**5** should be weak, which is consistent with the thermomagnetic data. As can be seen from Fig. 3, intermolecular antiferromagnetic exchange interactions between unpaired electrons of the paramagnetic centers appear in the temperature dependences of the effective magnetic moment (μ_{eff}) for the compounds under consideration at temperatures below 10—20 K. The structural data suggest that these interactions should be weaker in the crystals containing $[Co(SQ)_2(IN)_2]$ molecules, in which the nitroxyl groups point toward the chelate rings (see Fig. 2, *b*). In the solid phases of **1** and **2** (the packing motif of the coordination molecules is the same as in the crystals of **3**—**5**), the intermolecular distances between the N—O groups should be shorter due to the presence of two N—O groups in the nitroxide. Actually, these distances in the structures of **1** and **2** are shorter than those in **3**—**5**. However, in the crystals of the mixed-ligand complexes with NIT, the shortest distances between the O atoms of adjacent N—O groups are quite large (3.258 and 3.215 Å for compounds **1** and **2**, respectively). Therefore, the main interactions between unpaired electrons in the solid phases of the complexes should be located inside the heterospin molecules.

The main magnetic effect observed in the experimental temperature dependences of μ_{eff} for solvates **1**—**5** is valence tautomerism, resulting in that μ_{eff} substantially increases as the complexes are heated to temperatures above 250—300 K (see Fig. 3). The values of μ_{eff} in the range of 100—250 K for solvates **2** and **4** with MeCN (~3.0—3.1 μ_B; μ_B is Bohr magneton) are in good agreement with the theoretical value for paramagnetic particles, in which three unpaired electrons separated by an extended system of chemical bonds (due to which the interactions are weak) make a contribution to the magnetic moment. This corresponds to the valence tautomer $[Co^{III}(SQ)(Cat)L_2]$. This tautomer contains Co^{III} ions in the low-spin d^6 state, one catecholate ligand, one semiquinolate ligand with the spin $S = 1/2$, and two nitroxides with $S = 1/2$. An increase in the temperature to >250—300 K leads to a considerable increase in μ_{eff}, which is indicative of an increase in the fraction of the valence tautomer $[Co^{II}(SQ)_2L_2]$ in the equilibrium system $[Co^{III}(SQ)(Cat)L_2] \rightleftarrows [Co^{II}(SQ)_2L_2]$. For five weakly interacting paramagnetic centers, one of which is with $S = 3/2$ and four other centers are with $S = 1/2$, and the *g* factor equal to 2, the minimum spin-only value of μ_{eff} for all centers was theoretically estimated at 5.20 μ_B. The experimental values of μ_{eff} at 350 K do not reach a plateau, *i.e.*, the transition to the valence tautomer corresponding to the high-spin state is not completed. It was impossible to heat solvates **1**—**5** to high temperatures because this caused the decomposition of the compounds. However, even at 350 K, the effective magnetic moments are equal or even higher than the theoretical estimate of the minimum spin-only value (5.20 μ_B), which can be attributed to the orbital contribution to the magnetic susceptibility typical of Co^{II} in the octahedral environment and the *g* factors larger than 2.

For solvates **1**, **3**, and **5** (which, as mentioned above, are very unstable after the separation from the mother liquor), the experimental curves $\mu_{eff}(T)$ lie higher than the curves for the kinetically more stable solvates with MeCN. This is a consequence of the partial loss of the solvent molecules from the solid phases of complexes **1**, **3**, and **5**.

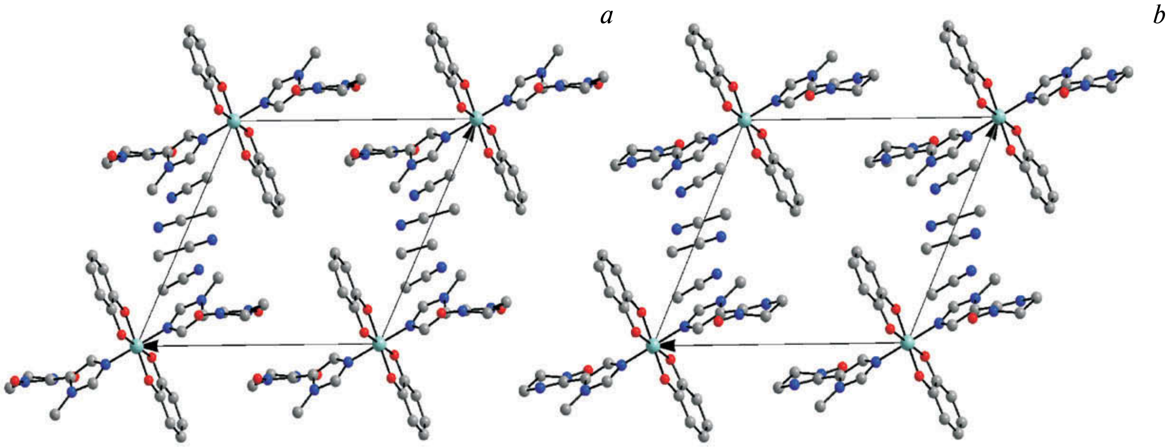

Fig. 2. Molecular packings in the solid phases of solvates **2** (*a*) and **4** (*b*).

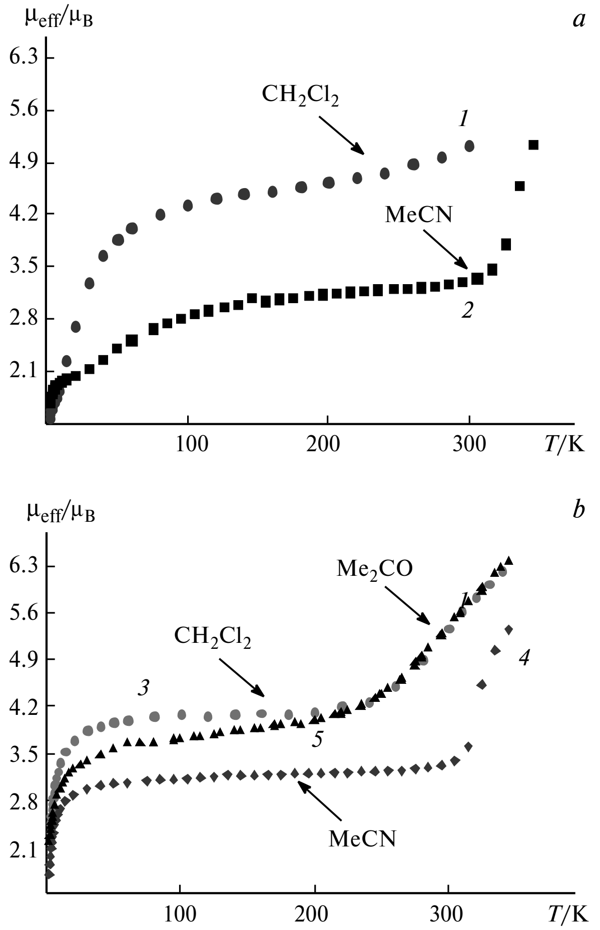

Fig. 3. Temperature dependences of the effective magnetic moment (μ_{eff}) for $[Co(SQ)_2(NIT)_2]\cdot 8CH_2Cl_2$ (*1*), $[Co(SQ)_2(NIT)_2]\cdot 4MeCN$ (*2*) (*a*) and $[Co(SQ)_2(IN)_2]\cdot 2CH_2Cl_2\cdot C_6H_{14}$ (*3*), $[Co(SQ)_2(IN)_2]\cdot 4MeCN$ (*4*), $[Co(SQ)_2(IN)_2]\cdot 5Me_2CO$ (*5*) (*b*).

The experimental curves $\mu_{eff}(T)$ for compounds **1**, **3**, and **5** calculated taking into account the loss of the solvent molecules have a plateau in the region of ~100—250 K close to that observed for solvates **2** and **4**, which are more resistant to decomposition. This is confirmed by the curves $\mu_{eff}(T)$ for the freshly prepared sample of $[Co(SQ)_2(IN)_2]\cdot 5Me_2CO$ and its desolvated product shown in Fig. 4. It can be seen that the curve $\mu_{eff}(T)$ for the freshly prepared sample, for which χ_M was calculated with the use of the molar weight of the non-desolvated $[Co(SQ)_2(IN)_2]\cdot 5Me_2CO$, lies substantially higher than the analogous curve for the desolvated complex after storage *in vacuo* (see Fig. 4), for which χ_M was calculated with the use of the smaller molar weight corresponding to $[Co(SQ)_2(IN)_2]$.

With the aim of preparing solvates of $[Co(SQ)_2(NIT)_2]$ and $[Co(SQ)_2(IN)_2]$ kinetically more resistant to decomposition, we made attempts to carry out the reactions of $Co(SQ)_3$ with NIT and IN in higher-boiling-point solvents, such as cumene, *o*-xylene, ethylbenzene, toluene, 1,1-diethoxyethane, and nitromethane. However, we failed to crystallize individual phases even from very small volumes of these solvents. Nevertheless, the thermomagnetic analysis for solvates **1—5** unambiguously showed that all the mixed-ligand heterospin complexes under study exhibit effects of valence tautomerism. For these complexes, the transition temperatures, *viz.*, the maxima in the change in dμ/d*T*, are observed in the range of 300—350 K. The transition temperature and the sharpness of the transitions are influenced by the incorporated solvent (see Fig. 3, *b*).

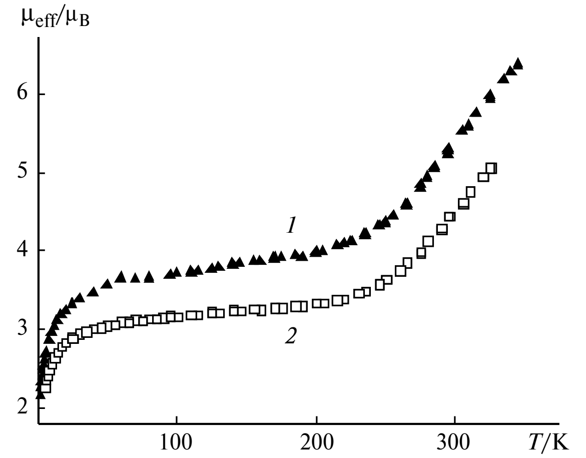

Fig. 4. Temperature dependences of the effective magnetic moment (μ_{eff}) for the freshly prepared complex $[Co(SQ)_2(IN)_2]\cdot 5Me_2CO$ (*1*) and the desolvated complex $[Co(SQ)_2(IN)_2]$ (*2*).

To sum up, it can be concluded that cobalt semiquinolate can be used in the reactions with imino and nitronyl nitroxides for the synthesis of heterospin mixed-ligand complexes exhibiting valence tautomerism. According to the thermomagnetic analysis for solvates **1—5** in the range of 2—350 K, these effects are manifested at ~20 °C. It should also be noted that the solvent molecules included in the solid phase have a particular effect on the magnetic anomaly temperature.

Experimental

The radicals 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (NIT) and the imine analog of NIT, *viz.*, 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (IN), used for the synthesis of the complexes were prepared according to a known procedure.[69]

Bis(3,6-di-*tert*-butylsemiquinolato)bis[4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl]cobalt(II) octakis(dichloromethane) solvate, $[Co(SQ)_2(NIT)_2]\cdot 8CH_2Cl_2$ (1). A mixture of $Co(SQ)_3$ (0.1 g, 0.14 mmol) and NIT (0.066 g, 0.28 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was filtered, hexane (5 mL) was added to the filtrate, and the mixture was kept at

−18 °C for 24 h. Dark-green crystals suitable for X-ray diffraction that formed were filtered off and washed with cold hexane. The elemental analysis data for the product, which was filtered and dried in air, were reproducibly consistent with the loss of all solvent molecules. The yield was 15—20% based on $Co(SQ)_2(NIT)_2$. Found (%): C, 61.0; H, 7.6; N, 11.8. For the fully desolvated product $C_{50}H_{74}N_8CoO_8$, calculated (%): C, 61.6; H, 7.6; N, 11.5.

Bis(3,6-di-*tert*-butylsemiquinolato)bis[4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl]cobalt(II) tetrakis(acetonitrile) solvate, $[Co(SQ)_2(NIT)_2] \cdot 4CH_3CN$ (2). The complex was synthesized by analogy with compound **1** using MeCN (30 mL) as the starting solvent. The yield was 20—25% based on $[Co(SQ)_2(NIT)_2]$. Found (%): C, 60.8; H, 7.6; N, 11.3. For the fully desolvated product $C_{50}H_{74}N_8CoO_8$, calculated (%): C, 61.6; H, 7.6; N, 11.5.

Bis(3,6-di-*tert*-butylsemiquinolato)bis[4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl]cobalt(II) pentakis(2-oxopropane) solvate, $[Co(SQ)_2(IN)_2] \cdot 5Me_2CO$ (3). A mixture of $Co(SQ)_3$ (0.03 g, 0.042 mmol) and IN (0.018 g, 0.083 mmol) was dissolved in acetone (4 mL) at ~20 °C. The resulting solution was filtered, and the filtrate was kept at −18 °C for 24 h. Dark-brown crystals that formed were filtered off and washed with cold acetone. The yield was 60% based on $Co(SQ)_2(IN)_2$. Found (%): C, 63.9; H, 8.6; N, 11.7. For the fully desolvated product $C_{50}H_{74}N_8CoO_6$, calculated (%): C, 63.7; H, 7.9; N, 11.9.

Bis(3,6-di-*tert*-butylsemiquinolato)bis[4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl]cobalt(II) bis(dichloromethanehexane) solvate, $[Co(SQ)_2(IN)_2] \cdot 2CH_2Cl_2 \cdot C_6H_{14}$ (5). A mixture of $Co(SQ)_3$ (0.05 g, 0.07 mmol) and IN (0.03 g, 0.14 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was filtered, and hexane (5 mL) was added to the filtrate. The reaction mixture was kept at −18 °C. After 24 h, dark-green crystals suitable for X-ray diffraction precipitated. The crystals were filtered off and washed with cold hexane. The yield was 15—20% based on $Co(SQ)_2(IN)_2$. Found (%): C, 63.7; H, 7.8; N, 12.0. For the fully desolvated product $C_{50}H_{74}N_8CoO_6$, calculated (%): C, 63.7; H, 7.9; N, 11.9.

Bis(3,6-di-*tert*-butylsemiquinolato)bis[4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl]cobalt(II) tetrakis(acetonitrile) solvate, $[Co(SQ)_2(IN)_2] \cdot 4CH_3CN$ (4). The complex was synthesized by analogy with compound **5** using MeCN (30 mL) as the solvent. The yield was 20—25% based on $Co(SQ)_2(IN)_2$. Found (%): C, 62.9; H, 7.7; N, 11.5. For the fully desolvated product $C_{50}H_{74}N_8CoO_6$, calculated (%): C, 63.7; H, 7.9; N, 11.9.

X-ray diffraction study. The X-ray diffraction data sets were collected on a SMART APEX CCD diffractometer (Bruker AXS) (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, absorption corrections were applied with the use of the Bruker SADABS software, version 2.10). Due to the presence of a large number of solvent molecules, the crystals were unstable, and the X-ray diffraction data were collected from crystals protected with an epoxy resin layer (**2**—**4**) or from crystals placed in thin-walled glass capillaries (**1** and **5**). 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 H atoms were positioned geometrically and refined isotropically using the rigid-group approximation. All calculations were carried out with the use of the Bruker Shelxtl Version 6.14 software. The crystallographic characteristics of the complexes are given in Table 1. Single crystals of **1**—**5** for X-ray diffraction studies were selected as described above.

Magnetic properties of the complexes were measured on a MPMSXL SQUID magnetometer in the temperature range of 5—350 K in a magnetic field of 5 kOe. The paramagnetic terms of the magnetic susceptibility (χ) were evaluated taking into account the diamagnetic contribution, which was estimated from the Pascal constants. The effective magnetic moment (μ_{eff}) was calculated by the equation

$$\mu_{eff} = \left(\frac{3k}{N_A \beta^2} \cdot \chi T \right)^{1/2} \approx (8\chi T)^{1/2},$$

where N_A is Avogadro′s number, β is the Bohr magneton, and *k* is the Boltzmann constant. The correction for the temperature-independent paramagnetism was not applied.

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References

1. S. S. Eaton, G. R. Eaton, *Coord. Chem. Rev.*, 1978, **26**, 207.
2. G. A. Abakumov, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1979, **24**, 156 (in Russian).
3. Yu. Zolotov, O. Petrukhin, V. Nagy, L. Volodarsky, *Anal. Chim. Acta*, 1980, **115**, 1.
4. S. V. Larionov, in *Imidazoline Nitroxides. Synthesis, Properties and Applications*, Ed. L. B. Volodarsky, CRC Press, Boca Raton, Florida, 1988, p. 81.
5. S. S. Eaton, G. R. Eaton, *Coord. Chem. Rev.*, 1988, **83**, 29.
6. A. Caneschi, D. Gatteschi, P. Rey, *Progr. Inorg. Chem.*, 1991, **39**, 331.
7. O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, 1993, 380 pp.
8. R. S. Drago, *Coord. Chem. Rev.*, 1980, **32**, 97.
9. S. V. Larionov, *Zh. Strukt. Khim.*, 1982, **23**, 125 [*J. Struct. Chem. (USSR)* (*Engl. Transl.*), 1982, **23**, 594].
10. L. B. Volodarsky, V. A. Reznikov, V. I. Ovcharenko, *Synthetic Chemistry of Stable Nitroxides*, CRC Press, Boca Raton, Florida, 1994, 225 p.
11. V. I. Ovcharenko, A. B. Gel′man, V. N. Ikorskii, *Zh. Strukt. Khim.*, 1989, **30**, 142 [*J. Struct. Chem. (USSR)* (*Engl. Transl.*), 1989, **30**, 815].
12. V. I. Ovcharenko, Dr. Sc. (Chem.) Thesis, A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1992, 376 pp. (in Russian).
13. S. V. Larionov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1990, **3**, 34 [*Bull. Sib. Branch Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1990, **3**, 38].
14. J. S. Miller, *Adv. Mater.*, 1994, **6**, 322.
15. V. I. Ovcharenko, R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1999, **68**, 345].

16. H. Iwamura, K. Inoue, T. Hayamizu, *Pure Appl. Chem.*, 1996, **68**, 243.
17. V. I. Ovcharenko, K. Yu. Maryunina, S. V. Fokin, G. V. Romanenko, V. N. Ikorskii, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2304 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2406].
18. D. Luneau, P. Rey, *Coord. Chem. Rev.*, 2005, **249**, 2591.
19. D. Luneau, A. Borta, Y. Chumakov, J.-F. Jacquot, E. Jeanneau, C. Lescop, P. Rey, *Inorg. Chim. Acta*, 2008, **361**, 3669.
20. A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392.
21. H. Iwamura, K. Inoue, in *Magnetism: Molecules to Materials II. Molecule-Based Materials*, Eds J. S. Miller, M. Drillon, Wiley-VCH, Weinheim, 2001, p. 61.
22. H. Oshio, T. Ito, *Coord. Chem. Rev.*, 2000, **198**, 329.
23. L. Ouahab, *Coord. Chem. Rev.*, 1998, **178—180**, 1501.
24. O. Sato, J. Tao, Y-Z. Zhang, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 2152.
25. O. Kahn, *Acc. Chem. Res.*, 2000, **33**, 647.
26. P. Rey, V. I. Ovcharenko, in *Magnetism: Molecules to Materials IV*, Eds J. S. Miller, M. Drillon, Wiley-VCH, New York, 2003, p. 41.
27. K. E. Vostrikova, *Coord. Chem. Rev.*, 2008, **252**, 1409.
28. E. Yu. Fursova, V. I. Ovcharenko, *Ross. Khim. Zh. (Zh. Ross. Khim. Obshch. im. D. I. Mendeleeva)*, 2009, **53**, No. 1, 23 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2009, **79**, 2731].
29. D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, 2006, 395 p.
30. D. Gatteschi, R. Sessoli, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 268.
31. E. Yu. Fursova, Dr. Sc. (Chem.) Thesis, International Tomography Center, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2010, 350 pp. (in Russian).
32. V. I. Ovcharenko, in *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, Ed. R. Hicks, Wiley-VCH, New York, 2010, p. 461.
33. E. Yu. Fursova, O. V. Kuznetsova, V. I. Ovcharenko, G. V. Romanenko, A. S. Bogomyakov, M. A. Kiskin, I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 1738 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1805].
34. C. G. Pierpont, R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
35. C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331.
36. C. G. Pierpont, S. Kitagawa, in *Inorganic Chromotropism*: *Basic Concepts and Applications of Colored Materials*, Ed. Y. Fukuda, Elsevier, Tokyo, 2007, p. 116.
37. A. I. Poddel'sky, V. K. Cherkasov, G. A. Abakumov, *Coord. Chem. Rev.*, 2009, **253**, 291.
38. Yu. V. Rakitin, N. V. Nemtsev, A. V. Lobanov, G. A. Abakumov, V. M. Novotortsev, V. T. Kalinnikov, *Koord. Khim.,* 1982, **8**, 1189 [*Sov. J. Coord. Chem.* (*Engl. Transl.*), 1982, **8**].
39. G. A. Abakumov, V. K. Cherkasov, M. P. Bubnov, O. G. Ellert, Yu. V. Rakitin, L. N. Zakharov, Yu. T. Struchkov, Yu. N. Saf´yanov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2315 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.* (*Engl. Transl.*), 1992, **41**, 1813].
40. A. V. Piskunov, G. K. Fukin, Yu. A. Kurskii, V. K. Cherkasov, G. A. Abakumov, *Inorg. Chem. Commun.*, 2005, **239**, 339.
41. V. I. Ovcharenko, E. V. Gorelik, S. V. Fokin, G. V. Romanenko, V. N. Ikorskii, A. V. Krashilina, V. K. Cherkasov, G. A. Abakumov, *J. Am. Chem. Soc.*, 2007, **129**, 10512.
42. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
43. R. M. Buchanan, C. G. Pierpont, *J. Am. Chem. Soc.*, 1980, **102**, 4951.
44. G. A. Abakumov, V. K. Cherkasov, M. P. Bubnov, O. G. Ellert, Zh. V. Dobrokhotova, L. N. Zakharov, Yu. T. Struchkov, *Dokl. Akad. Nauk*, 1993, **328**, 332 [*Dokl. Chem.* (*Engl. Transl.*), 1993, **328**, 12].
45. D. M. Adams, A. Dei, A. L. Rheingold, D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 880.
46. O.-S. Jung, C. G. Pierpont, *Inorg. Chem.*, 1994, **33**, 2227.
47. S. A. Attia, S. Bhattacharya, C. G. Pierpont, *Inorg. Chem.*, 1995, **34**, 4427.
48. S. A. Attia, C. G. Pierpont, *Inorg. Chem.*, 1995, **34**, 1172.
49. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216—217**, 99.
50. H. Ohtsu, K. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 6301.
51. D. A. Shultz, J. C. Sloop, G. J. Washington, *Org. Chem.*, 2006, **71**, 9104.
52. D. A. Shultz, in *Magnetism: Molecules to Materials, II. Molecular-Based Materials*, Ed. J. S. Miller, M. Drillon, Wiley-VCH, New York, 2001, p. 281.
53. D. N. Hendrickson, C. G. Pierpont, in *Topics in Current Chemistry*, Eds P. Gütlich, H. A. Goodwin, Springer-Verlag, Berlin—Heidelberg, 2004, p. 63.
54. P. Gütlich, A. Dei, *Angew. Chem., Int. Ed. Engl.*, 1997, **37**, 2734.
55. O.-S. Jung, D. H. Jo, Y.-A. Lee, B. J. Conklin, C. G. Pierpont, *Inorg. Chem.*, 1997, **36**, 19.
56. A. Caneschi, A. Dei, F. Fabrizi de Biani, P. Gütlich, V. Ksenofontov, G. Levchenko, A. Hoefer, F. Renz, *Chem. Eur. J.*, 2001, **7**, 3926.
57. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, *Science,* 2001, **294**, 1488.
58. J.-E. Moser, *Nat. Mater.*, 2005, **4**, 723.
59. K. Tagami, M. J. Tsukada, *Phys. Chem. B*, 2004, **108**, 6441.
60. J. Yuasa, T. Suenobu, S. J. Fukuzumi, *Phys. Chem. A*, 2005, **109**, 9356.
61. Y. Suenaga, C. G. Pierpont, *Inorg. Chem.*, 2005, **44**, 6183.
62. E. Evangelio, D. Ruiz-Molina, *Eur. J. Inorg. Chem.*, 2005, **15**, 2957.
63. O. J. Sato, *Photochem. Photobiol. C: Photochem. Rev.*, 2004, **5**, 203.
64. A. Dei, D. Gatteschi, C. Sangregorio, L. Sorace, *Acc. Chem. Res.*, 2004, **37**, 827.
65. O.-S. Jung, C. G. Pierpont, *J. Am. Chem. Soc.*, 1994, **116**, 1127.
66. J.-F. Letard, P. Guionneau, L. Goux-Capes, in *Topics in Current Chemistry*, Ed. P. Gütlich, H. A. Goodwin, Springer-Verlag, Berlin—Heidelberg, 2004, p. 221.
67. G. A. Abakumov, V. I. Nevodchikov, *Dokl. Akad. Nauk SSSR*, 1982, **266**, 1407 [*Dokl. Chem.* (*Engl. Transl.*), 1982, **266**, 12].
68. C. W. Lange, M.Foldeaki, V. I. Nevodchikov, K. Cherkasov, G. A. Abakumov, C.G. Pierpont, *J. Am. Chem. Soc.*, 1992, **114**, 4220.
69. V. Ovcharenko, E. Fursova, G. Romanenko, I. Eremenko, E. Tretyakov, V. Ikorskii, *Inorg. Chem.*, 2006, **45**, 5338.

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