Synthesis and structures of five-coordinate bis-*o*-iminobenzosemiquinone complexes $M(ISQ—R)_2X$ (X = Cl, Br, I, or SCN; M = Co^{III}, Fe^{III}, or Mn^{III})

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New five-coordinate complexes $Co(ISQ\text{-}Pr^i)_2Cl$, $Co(ISQ\text{-}Me)_2Cl$, $Co(ISQ\text{-}Me)_2I$, $Co(ISQ\text{-}Me)_2(SCN)$, $Mn(ISQ\text{-}Pr^i)_2Cl$, and $Fe(ISQ\text{-}Me)_2Br$ (ISQ-Pr^i and ISQ-Me are the 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)- and 4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzosemiquinone radical anions, respectively) were synthesized. The complexes were characterized by UV-Vis and IR spectroscopy and magnetochemistry. The molecular structures of the $Fe(ISQ\text{-}Me)_2Br$ and $Mn(ISQ\text{-}Pr^i)_2Cl$ complexes were established by X-ray diffraction. The singlet ground state (S = 0) of the cobalt complexes is caused by antiferromagnetic coupling between the unpaired electrons of the radical ligands (S = 1/2) through the fully occupied atomic orbitals of low-spin cobalt(III) (d^6, S = 0). The effective magnetic moments of the complexes at 10 K are 0.18 μ_B for $Co(ISQ\text{-}Pr^i)_2Cl$ and 0.16 μ_B for $Co(ISQ\text{-}Me)_2I$. The ground state of the manganese complex is triplet (S = 1). Two unpaired electrons of the *o*-iminobenzosemiquinone ligands are strongly antiferromagnetically coupled with two of four unpaired electrons of high-spin manganese(III) (d^4, S = 2).

Key words: cobalt, iron, manganese, *o*-iminobenzoquinone, *o*-iminobenzosemiquinone, X-ray diffraction, magnetochemistry.

Abundant data on *o*-semiquinone complexes have been accumulated.[1,2] Studies of metal complexes with *o*-iminobenzoquinone ligands (analogs of *o*-benzoquinones) are of considerable interest because *o*-iminobenzoquinones have distinguishing features due to which such studies extend the range of related compounds and add to our knowledge of this class of complexes.

Unlike *o*-quinones, *o*-iminoquinones are asymmetric, and the presence of the nitrogen atom allows one to investigate the spin density distribution in the chelate ring. The use of *o*-iminosemiquinone as a spin-labeled ligand in metal complexes helps in solving structural-dynamic problems[3] and makes it possible to determine the spatial arrangement of ligands containing magnetic nuclei with respect to the plane of the *o*-iminosemiquinone plane.[4] At the same time, *o*-iminosemiquinones, like *o*-semiquinones, serve as magnetic centers. From this standpoint, investigation of spin couplings between ligands and/or between ligands and metals are of interest.

The steric hindrance of the metal centers in complexes can be varied over a wide range by introducing various substituents at the nitrogen atom. For example, *o*-iminobenzoquinones containing the unsubstituted phenyl substituent at the nitrogen atom form tris-ligand transition metal complexes, which are very similar to *o*-semiquinone derivatives.[5—7]

The introduction of alkyl substituents at positions 2 and 6 leads to stabilization of low-coordinated cobalt and manganese compounds, in which these metals have an unusual coordination number of 4.[8,9] Since the metal atoms in these complexes are coordinatively unsaturated, small molecules and atoms can additionally be bonded to form five-coordinate complexes.[8—10] The preparation of mixed-ligand complexes of composition ML_2X, where X is halogen, offers possibilities for the synthesis of complexes containing radical ligands of different nature.

The aim of the present study was to synthesize and characterize five-coordinate cobalt, iron, and manganese complexes with the sterically hindered 4,6-di-*tert*-butyl-*N*-aryl-*o*-iminobenzosemiquinone ligands (aryl is 2,6-diisopropylphenyl or 2,6-dimethylphenyl). The resulting compounds were compared with the known cobalt com-

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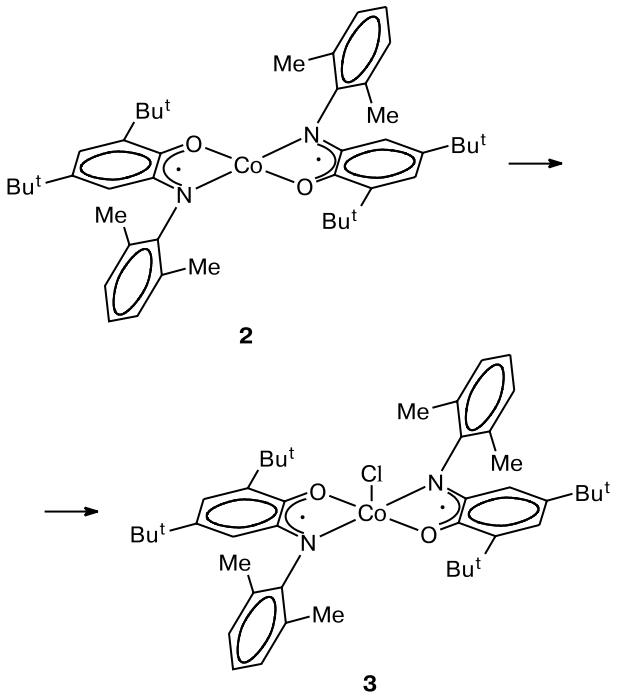
plexes $Co(ISQ)_2Cl$ and $Co(ISQ)_2I$ and the iron complex $Fe(ISQ)_2Cl$ containing the less sterically hindered 4,6-di-*tert*-butyl-*N*-phenyl-*o*-iminobenzoquinone ligand.[11,12]

Results and Discussion

Earlier, we have described the four-coordinate cobalt(II) bis-*o*-iminobenzosemiquinone complexes $Co(ISQ\text{-}Pr^i)_2$ (**1**) and $Co(ISQ\text{-}Me)_2$ (**2**).[8] Steric hindrance at the nitrogen atoms of the *o*-iminoquinone ligands in the direct environment of the central metal atom excludes the possibility of coordination of the third bidentate ligand (*o*-iminoquinone). At the same time, the possibility of introducing small monodentate ligands into the coordination sphere of metal atoms is retained.

Earlier,[8] we have found that sterically hindered complex **2** can react with chlorine-containing solvents to form the chloride-containing cobalt(III) bis-*o*-iminobenzosemiquinone complex $Co(ISQ\text{-}Me)_2Cl$ (**3**) (Scheme 1).

Scheme 1



Reagents and conditions: $h\nu$, CH_2Cl_2, hexane.

By contrast, the analogous cobalt(III) complex $Co(ISQ\text{-}Pr^i)_2Cl$ (**4**) is not generated from sterically more hindered complex **1** in the presence of chlorine-containing solvents.

Alternatively, chlorine-containing cobalt bis-*o*-iminobenzosemiquinone complex **3** can be synthesized by the reaction of anhydrous cobalt(II) chloride with (*o*-iminobenzosemiquinone)thallium(I) (**5**) in the presence of free *o*-iminobenzoquinone (Scheme 2).[8]

Scheme 2

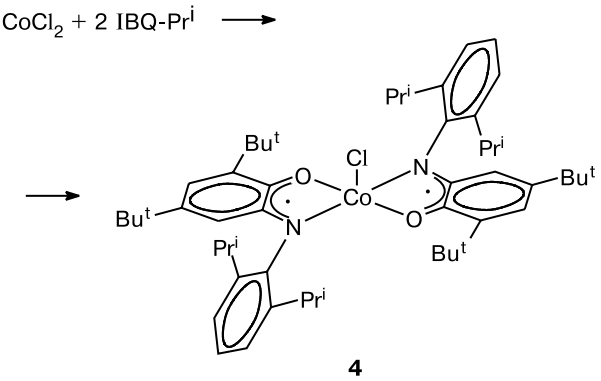
$$CoCl_2 + IBQ\text{-}Me + Tl(ISQ\text{-}Me) \xrightarrow{\mathbf{5}} Co(ISQ\text{-}Me)_2Cl \quad (\mathbf{3})$$

$$CoCl_2 + IBQ\text{-}Pr^i + Tl(ISQ\text{-}Pr^i) \xrightarrow{\mathbf{6}} Co(ISQ\text{-}Pr^i)_2 + Co(ISQ\text{-}Pr^i)_2Cl \quad (\mathbf{1}, \mathbf{4})$$

However, the reaction with the use of isopropyl-substituted iminoquinone gives a mixture of five-coordinate complex **4** and four-coordinate complex **1** (see Scheme 2). The reaction products cannot be preparatively separated because of their similar solubility.

A convenient procedure for the synthesis of complex **4** (without an impurity of **1**) is based on the reaction of cobalt(II) chloride with *o*-iminobenzoquinone $IBQ\text{-}Pr^i$ in THF (Scheme 3).

Scheme 3

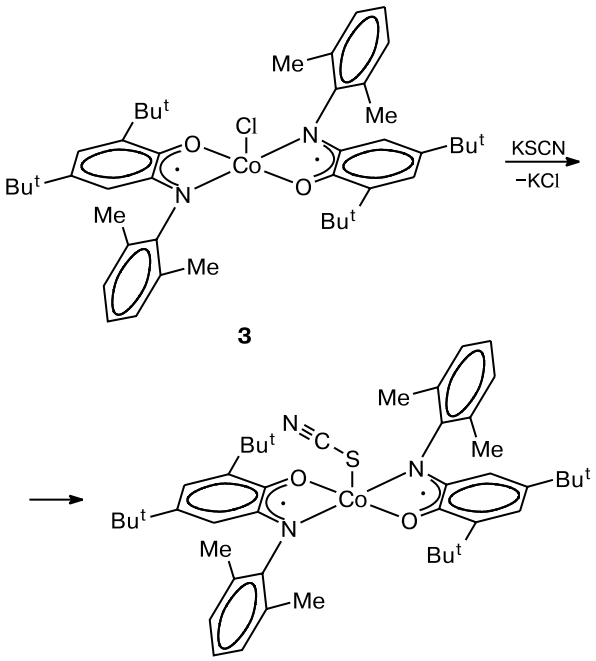


The chloride ion in compound **3** is chemically active and can be replaced with another anionic ligand. This is exemplified by the reaction of compound **3** with potassium rhodanide in a THF—methanol mixture (Scheme 4). The replacement of the anion gives rise to the rhodano-bis-*o*-iminobenzosemiquinone cobalt(III) complex (**7**).

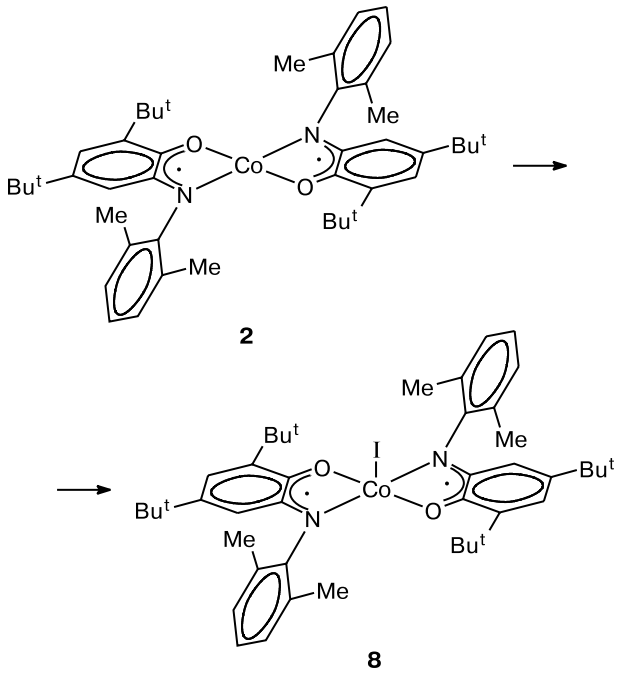
The addition of iodine to a solution of complex **2** (Scheme 5) also leads to oxidation of cobalt(II) to cobalt(III) and the formation of the five-coordinate complex $Co(ISQ\text{-}Me)_2I$ (**8**).

Unlike cobalt halides, manganese(II) and iron(II) halides react with thallium(I) *o*-iminobenzosemiquinolate in the presence of *o*-iminobenzoquinone to give the target five-coordinate complexes in good yields regardless of the nature of substituents in the *N*-aryl moiety. This method was used to synthesize the $Mn(ISQ\text{-}Pr^i)_2Cl$ (**9**) and $Fe(ISQ\text{-}Me)_2Br$ (**10**) complexes (Scheme 6).

Scheme 4



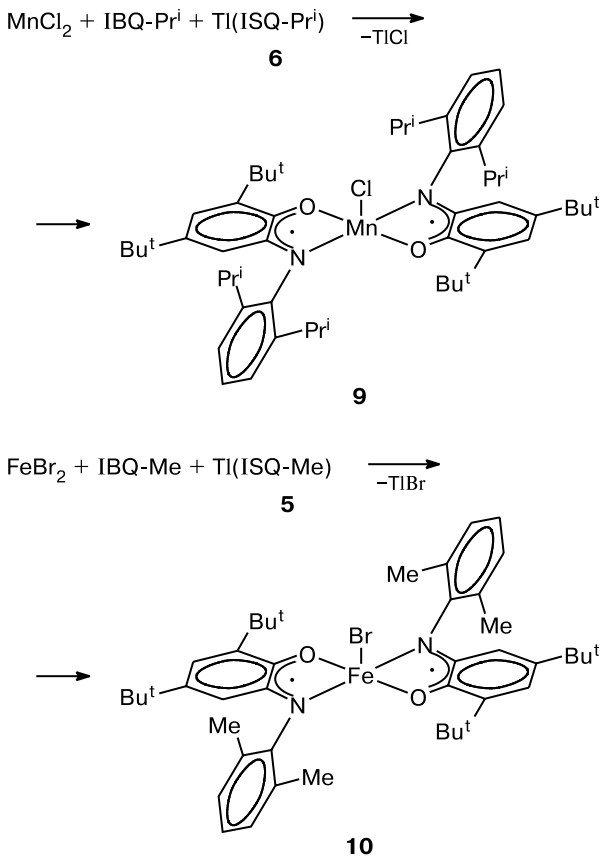
Scheme 5



Reagents and conditions: I_2, toluene.

Compounds **3**, **4**, and **7**—**10** were isolated in individual form and characterized by IR spectroscopy, electronic absorption spectroscopy (EAS), and elemental analysis.

Scheme 6



The presence of the *o*-iminobenzoquinone ligands in the complexes is evidenced by a characteristic set of bands in the 700—1600 cm^{-1} region. The IR spectra of these complexes show intense stretching bands of C—O and C—N "one-and-a-half" bonds at 1450—1500 cm^{-1} characteristic of complexes containing the *o*-iminobenzosemiquinone radical-anionic ligands.[3—10]

The electronic absorption spectra of chloride-containing cobalt complexes **3** and **4** (Fig. 1, Table 1) show intense bands ($\varepsilon \approx 10^4$ L mol^{-1} cm^{-1}) at 675—680 and 840—846 nm, respectively. The electronic absorption spectra of these complexes are virtually identical to those of the analogous $Co(ISQ)_2Cl$ and $Co(ISQ)_2I$ complexes prepared in the study[11] (see Table 1).

The electronic absorption spectrum of manganese complex **9** shows a narrow intense band at 474 nm. The electronic absorption spectrum of iron complex **10** contains a broad intense absorption band with a maximum at 762 nm (Fig. 2).

Structures of complexes

The structure of $Co(ISQ\text{-}Me)_2Cl$ complex **3** has been described earlier.[8] The molecular structures of the man-

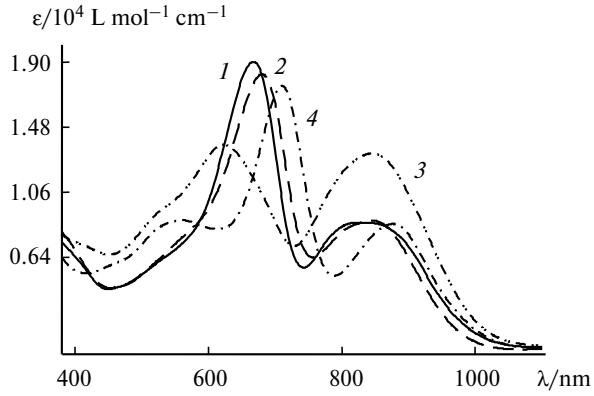


Fig. 1. Electronic absorption spectra of complexes **3** (*1*), **4** (*2*), **7** (*3*), and **8** (*4*) (toluene, 290 K).

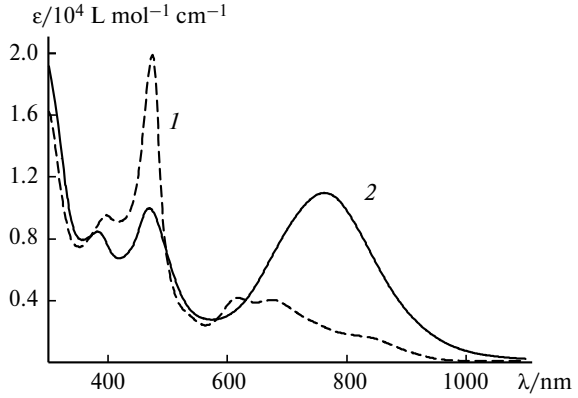


Fig. 2. Electronic absorption spectra of complexes **9** (*1*) and **10** (*2*) (toluene, 290 K).

Table 1. Parameters of the electronic absorption spectra of complexes **3**, **4**, **7**—**10**, $Co(ISQ)_2Cl$, and $Co(ISQ)_2I$*

Complex	Solvent	λ/nm (ε/L mol^{-1} cm^{-1})
$Co(ISQ\text{-}Me)_2Cl$ (**3**)	Toluene	352 (9270), 675 (18900), 840 (8700)
$Co(ISQ\text{-}Pr^i)_2Cl$ (**4**)	Toluene	353 (9400), 680 (18200), 846 (8370)
$Co(ISQ)_2Cl$*	CH_2Cl_2	672 (15000), 821 (13000)*
$Co(ISQ)_2I$*	CH_2Cl_2	566 (7800), 695 (18700), 884 (10300)*
$Co(ISQ\text{-}Me)_2(SCN)$ (**7**)	Toluene	624 (13500), 845 (12900)
$Co(ISQ\text{-}Me)_2I$ (**8**)	Toluene	350 (shoulder), 559 (8700), 710 (17500), 877 (8500)
$Mn(ISQ\text{-}Pr^i)_2Cl$ (**9**)	Toluene	396 (9500), 474 (19900), 617 (4140), 675 (4000), 839 shoulder (1630)
$Fe(ISQ\text{-}Me)_2Br$ (**10**)	Toluene	383 (8470), 469 (9900), 762 (10860)

* Published data.[11]

Table 2. Selected bond lengths (*d*) in molecules **9** and **10**

9		**10**	
Bond	*d*/Å	Bond	*d*/Å
Mn(1)—O(1)	1.876(2)	Fe(1)—O(1)	1.944(2)
Mn(1)—O(2)	1.872(2)	Fe(1)—O(2)	1.948(2)
Mn(1)—N(1)	1.949(3)	Fe(1)—N(1)	1.993(3)
Mn(1)—N(2)	1.944(3)	Fe(1)—N(2)	2.003(3)
Mn(1)—Cl(1)	2.2728(12)	Fe(1)—Br(1)	2.3755(7)
O(1)—C(1)	1.310(4)	O(1)—C(1)	1.298(3)
O(2)—C(27)	1.317(4)	O(2)—C(23)	1.296(3)
N(1)—C(6)	1.362(4)	N(1)—C(2)	1.339(3)
N(1)—C(15)	1.445(4)	N(1)—C(15)	1.445(4)
N(2)—C(32)	1.348(4)	N(2)—C(28)	1.343(3)
N(2)—C(41)	1.456(4)	N(2)—C(37)	1.436(3)
C(1)—C(2)	1.423(4)	C(1)—C(2)	1.421(4)
C(1)—C(6)	1.424(4)	C(1)—C(6)	1.442(4)
C(2)—C(3)	1.376(5)	C(2)—C(3)	1.374(4)
C(3)—C(4)	1.418(4)	C(3)—C(4)	1.419(4)
C(4)—C(5)	1.365(4)	C(4)—C(5)	1.355(4)
C(5)—C(6)	1.402(4)	C(5)—C(6)	1.417(5)
C(27)—C(28)	1.416(4)	C(23)—C(24)	1.427(4)
C(27)—C(32)	1.434(4)	C(23)—C(28)	1.449(4)
C(28)—C(29)	1.378(5)	C(24)—C(25)	1.362(4)
C(29)—C(30)	1.420(4)	C(25)—C(26)	1.426(4)
C(30)—C(31)	1.357(4)	C(26)—C(27)	1.365(4)
C(31)—C(32)	1.400(4)	C(27)—C(28)	1.415(4)

ganese complex $Mn(ISQ\text{-}Pr^i)_2Cl$ (**9**) and the iron complex $Fe(ISQ\text{-}Me)_2Br$ (**10**) are shown in Figs 3 and 4, respectively. Crystals of **9** suitable for X-ray diffraction contain one hexane molecule of crystallization per molecule **9**. In crystals of **10**, solvent molecules are absent. Selected bond lengths and bond angles for complexes **9** and **10** are given in Tables 2 and 3, respectively.

According to the X-ray diffraction data, compounds **9** and **10**, like **3**, have a distorted square-pyramidal geometry. The *o*-iminobenzosemiquinone ligands chelated to the central metal atom form the base of the pyramid, the oxygen and nitrogen atoms of the ligands being in *trans* positions. The halogen atom occupies the apex of the pyramid.

The C—O and C—N distances in the *o*-iminoquinone moiety vary in ranges characteristic of metal *o*-iminosemiquinone complexes.[5—13]

Compound	*d*/Å	
	C—O	C—N
9	1.310(4)	1.348(4)
	1.317(4)	1.362(4)
10	1.296(3)	1.339(3)
	1.298(3)	1.343(3)

The six-membered C(1)—C(6) and C(27)—C(32) rings in molecule **9** and the C(1)—C(6) and C(23)—C(28) rings in molecule **10** are characterized by a quinoid dis-

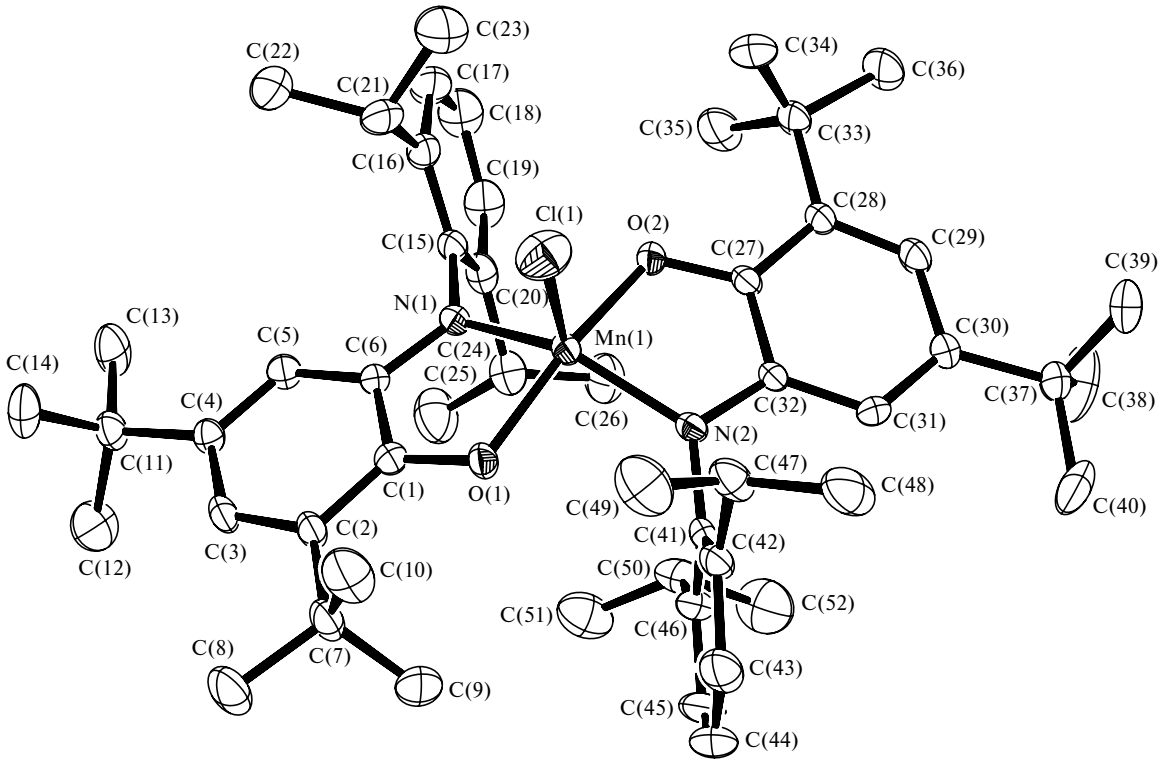


Fig. 3. Molecular structure of the $Mn(ISQ\text{-}Pr^i)_2Cl$ complex (**9**) (hydrogen atoms are omitted).

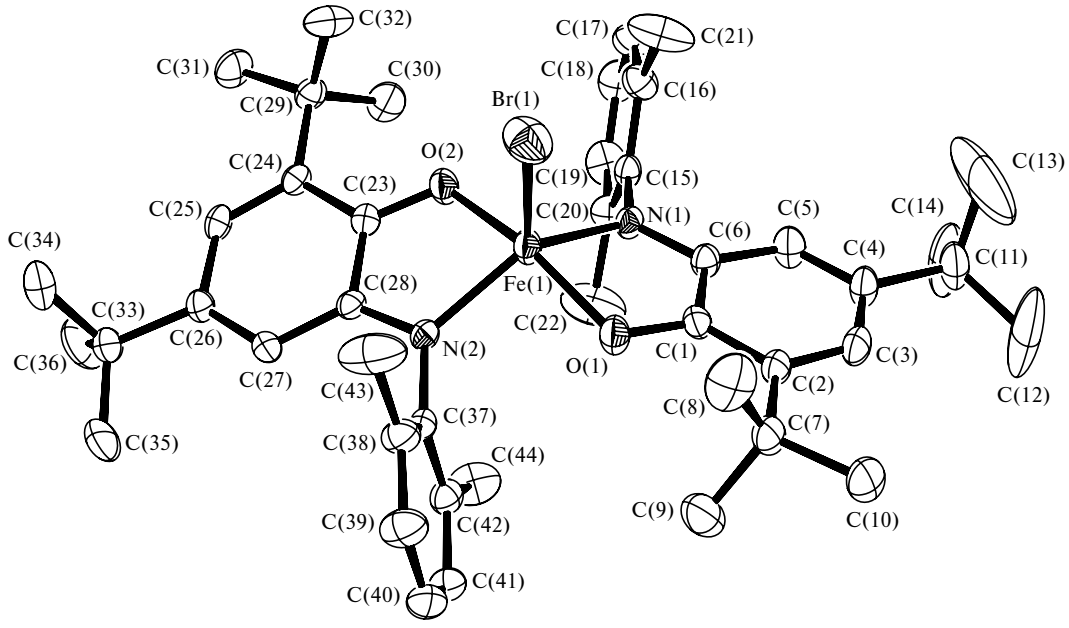


Fig. 4. Molecular structure of the $Fe(ISQ\text{-}Me)_2Br$ complex (**10**) (hydrogen atoms are omitted).

tortion typical of *o*-semiquinones and *o*-iminosemiquinones, in which the C—C bond lengths vary in the following order: three longer bonds—a short bond—a long bond—a short bond. For example, the C(1)—C(2), C(1)—C(6), and C(5)—C(6) distances in manganese complex **9** are 1.424(4), 1.423(4), and 1.402(4) Å, respectively, the C(2)—C(3) and C(4)—C(5) bonds are shorter (1.376(5) and 1.365(4) Å, respectively), whereas the C(3)—C(4) bond is elongated (1.418(4) Å).

The O(1)—Mn(1)—O(2) angle (Fig. 5, *a*) in complex **9** (165.43(10)°) is slightly smaller than the corresponding angle in cobalt complex $Co(ISQ\text{-}Me)_2Cl$ **3**

Table 3. Selected bond angles (ω) in molecules **9** and **10**

9		**10**	
Angle	ω/deg	Angle	ω/deg
O(1)—Mn(1)—O(2)	165.43(10)	O(1)—Fe(1)—O(2)	162.57(10)
N(1)—Mn(1)—N(2)	143.65(11)	N(1)—Fe(1)—N(2)	136.79(10)
O(1)—Mn(1)—N(1)	82.05(10)	O(1)—Fe(1)—N(1)	80.59(9)
O(2)—Mn(1)—N(2)	81.91(10)	O(2)—Fe(1)—N(2)	80.35(9)
O(1)—Mn(1)—N(2)	93.66(10)	O(1)—Fe(1)—N(2)	93.01(9)
O(2)—Mn(1)—N(1)	93.26(10)	O(2)—Fe(1)—N(1)	93.17(9)
O(1)—Mn(1)—Cl(1)	97.36(7)	O(1)—Fe(1)—Br(1)	98.03(7)
O(2)—Mn(1)—Cl(1)	97.22(8)	O(2)—Fe(1)—Br(1)	99.40(7)
N(1)—Mn(1)—Cl(1)	108.34(8)	N(1)—Fe(1)—Br(1)	110.32(7)
N(2)—Mn(1)—Cl(1)	108.01(8)	N(2)—Fe(1)—Br(1)	112.88(7)
C(1)—O(1)—Mn(1)	116.08(18)	C(1)—O(1)—Fe(1)	114.59(18)
C(27)—O(2)—Mn(1)	116.07(18)	C(23)—O(2)—Fe(1)	115.50(18)
C(6)—N(1)—C(15)	119.6(3)	C(6)—N(1)—C(15)	119.3(2)
C(6)—N(1)—Mn(1)	113.42(19)	C(6)—N(1)—Fe(1)	113.03(19)
C(15)—N(1)—Mn(1)	126.8(2)	C(15)—N(1)—Fe(1)	127.63(17)
C(32)—N(2)—C(41)	119.3(3)	C(28)—N(2)—C(37)	119.2(2)
C(32)—N(2)—Mn(1)	113.8(2)	C(28)—N(2)—Fe(1)	113.95(18)
C(41)—N(2)—Mn(1)	126.9(2)	C(37)—N(2)—Fe(1)	126.85(17)

(172.34(7)°). The N(1)—Mn(1)—N(2) angle (143.65(10)°) is also smaller than the N(1)—Co—N(2) angle in complex **3** (149.17(8)°). In the analogous cobalt complex $Co(ISQ)_2Cl$ containing the unsubstituted Ph fragments at the nitrogen atoms of the organic ligands, the corresponding angles are 163.57° for O—Co—O and 161.57° for N—Co—N.[11] In iron complex **10**, the O(1)—Fe(1)—O(2) angle decreases to 162.57(10)°, and the N(1)—Fe(1)—N(2) angle decreases to 136.79(10)° (Fig. 5, *b*).

A decrease in the N—Co—N angle is attributed to an increase in the steric effect of the Me substituents at positions 2 and 6 of the phenyl groups at the nitrogen atoms of the iminobenzosemiquinone moiety in cobalt complex **3** compared to the effect of the hydrogen atoms in the cobalt complex $Co(ISQ)_2Cl$ containing the unsubstituted *N*-phenyl groups.[11] An even stronger steric effect of the isopropyl substituents in the *N*-phenyl groups is observed in manganese complex **9**. The replacement of the chlorine atom (cobalt complex **3**) with bromine (iron complex **10**) also leads to a decrease in the N—Fe—N angle compared to the N—Co—N angle in complex **3**.

The Mn(1)—O(1) and Mn(1)—O(2) distances (1.872(2) and 1.876(2) Å, respectively) and the Mn(1)—N(1) and Mn(1)—N(2) distances (1.949(3) and 1.944(3) Å, respectively) in molecule **9** are longer than the analogous distances in the bis-ligand manganese(III) complex $Mn(ISQ\text{-}Pr^i)(AP\text{-}Pr^i)$ ($AP\text{-}Pr^i$ is 4,6-di-*tert*-butyl-*N*-(1,6-diisopropylphenyl)-*o*-amidophenoxide; Mn—O, 1.859(2) Å; Mn—N, 1.896(2) Å) with a coordi-

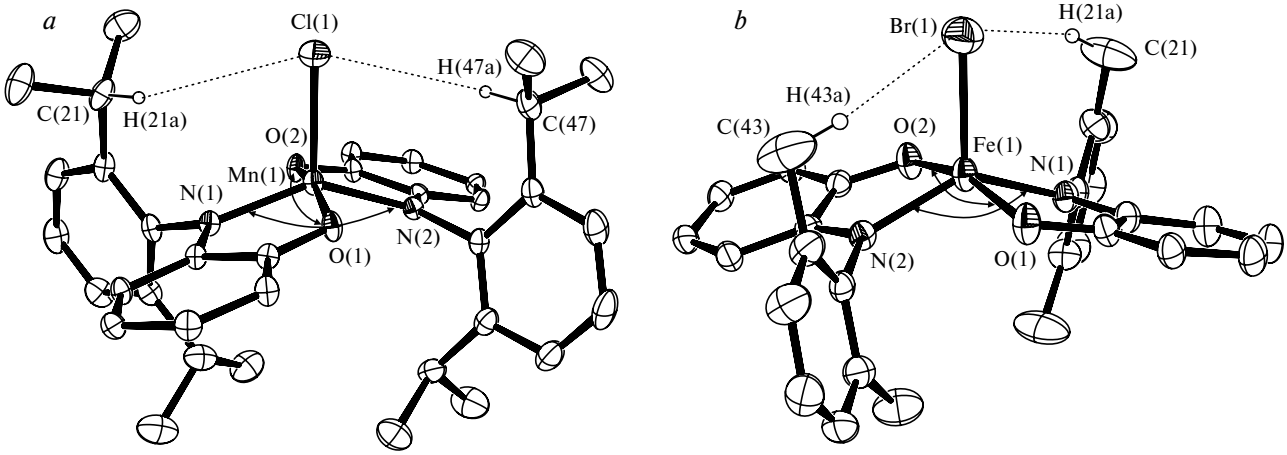


Fig. 5. Molecular structures of **9** (*a*) and **10** (*b*): O(1)—M—O(2), 65.43 (**9**) and 162.57 (**10**); N(1)—M—N(2), 143.65 (**9**) and 136.80 (**10**) (hydrogen atoms and *tert*-butyl groups are omitted).

nation number of 4.[9] At the same time, these distances differ only slightly from the corresponding Mn—O (aver., 1.872 Å) and Mn—N (aver., 1.920 Å) bond lengths in the manganese(III) complex Mn(ISQ-Pr^i)(AP-Pr^i)·THF with a coordination number of 5.[10] This is consistent with the difference in the ionic radii of Mn(III) in compounds with different coordination numbers.[14] In complex **10**, the Fe(1)—O(1), Fe(1)—O(2) (aver., 1.946(2) Å) and Fe(1)—N(1), Fe(1)—N(2) (aver., 1.998(2) Å) bond lengths are also slightly smaller than those in the tris-ligand complex $Fe(ISQ)_3$ (aver., 2.014(3) and 2.099(3) Å, respectively).[6] This is also consistent with a slight decrease in the covalent radius of iron(III) with decreasing coordination number.[14]

Magnetic properties

The temperature dependences of the magnetic characteristics of cobalt complexes **4** and **8** are shown in Fig. 6; for manganese complex **9**, in Fig. 7. In spite of the presence of two radical ligands, the magnetic moments of complexes **4** and **8** at 300 K are smaller than 1 μ_B (0.66 μ_B for **4** and 0.53 μ_B for **8**) and they approach zero (0.16—0.18 μ_B) as the temperature decreases to 10 K. The temperature dependences of the magnetic susceptibility of these complexes obey the Curie—Weiss law with the temperature-independent Van Vleck contribution $N\alpha$ (solid lines in Fig. 6):

$$\chi = \frac{C}{T - \theta} + N\alpha.$$

The optimum parameters of the equation are $C = 0.00505$, $\theta = -2.4$ K, and $N\alpha = 105 \cdot 10^{-6}$ for complex **4**, and $C = 0.00307$, $\theta = -6.0$ K, and $N\alpha = 180 \cdot 10^{-6}$ for complex **8**. The effective magnetic moments corresponding to the constants C are 0.2 μ_B and 0.16 μ_B for complexes **4** and **8**, respectively. Such small values of the magnetic moments indicate that the samples contain impurities with the spin $S = 1/2$. According to estimations, the percentage of these impurities is 1.3% for **4** and 0.8% for **8**.

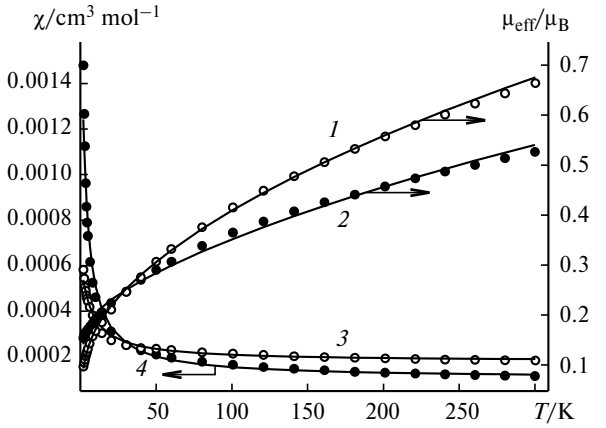


Fig. 6. Temperature dependences of the effective magnetic moments (μ_{eff}; *1*, *2*) and magnetic susceptibilities (χ; *3*, *4*) of cobalt complexes **4** (*1*, *3*) and **8** (*2*, *4*). The dotted curves show experimental data, and the solid curves indicate theoretical curves described by the equation $\chi = C/(T - \theta) + N\alpha$.

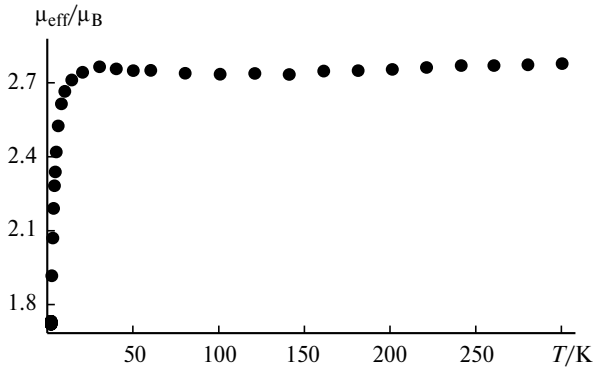


Fig. 7. Temperature dependence of the magnetic moment of the manganese complex Mn(ISQ-Pr^i)$_2$Cl (**9**).

The magnetic moment of manganese complex **9** at 300 K is 2.77 μ_B and, unlike the magnetic moments of the cobalt complexes, it remains virtually unchanged up to 20 K.

In the cobalt complexes, in which the low-spin cobalt(III) atom has a square-pyramidal geometry, d^6 ($S = 0$), and is coordinated by two *o*-iminosemiquinone ligands ($S_{rad} = 1/2$), the singlet ground state of the complexes is attributed to strong antiferromagnetic coupling between the unpaired electrons on π-MO of the ligands through the orbitals of the central atom. Such antiferromagnetic interactions are known for square-planar *o*-semiquinone and *o*-iminosemiquinone complexes of nickel, cobalt, and copper. The Ni(3,6-DBSQ)$_2$ complex is diamagnetic ($S = 0$) in the temperature range of 77—470 K,[15] like its *o*-iminosemiquinone analog Ni(ISQ)$_2$, which is characterized by the well-resolved ^{1}H NMR spectrum without paramagnetic shifts or broadening of the spectral lines.[5] In the square-planar complexes Co(ISQ-Pr^i)$_2$ (**1**) and Co(ISQ-Me)$_2$ (**2**), the strong antiferromagnetic coupling between the unpaired electrons of the ligands results in the doublet ground state ($S = 1/2$).[8] The bis-*o*-semiquinone complex Cu(3,6-DBSQ)$_2$ and the bis-*o*-iminosemiquinone complex Cu(ISQ)$_2$ exist in the ground doublet state with a low-lying temperature accessible quadruplet ($S = 3/2$).[5,15]

The effective magnetic moment of manganese complex **9** (2.77 μ_B) is similar to the spin-only value (2.83 μ_B) for systems containing two unpaired electrons on one center ($S = 1$). In this complex, the high-spin manganese(III) atom, d^4 ($S = 2$), has two unpaired electrons on the d_{xz} and d_{yz} atomic orbitals, which are strongly antiferromagnetically coupled with the unpaired electrons of two *o*-iminobenzosemiquinone ligands, which are local-

ized on π-MO and have the same symmetry as the above-mentioned AO of the metal aton.

Experimental

All operations associated with the synthesis and investigations of the properties of the complexes were performed in evacuated tubes in the absence of atmospheric oxygen and moisture. The solvents were purified and dried according to standard procedures.[16] 4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (IBQ-Pr^i) and 4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzoquinone (IBQ-Me) were prepared according to a procedure described earlier.[17]

The IR spectra were recorded on a Specord M-80 instrument in Nujol mulls. The electronic absorption spectra were measured on a Perkin—Elmer Lambda 25 UV-vis spectrometer (220—1100 nm range) at room temperature. The magnetic properties of complexes **4**, **8**, and **9** were studied in the temperature range of 5—300 K on a SQUID magnetometer with the use of an external magnetic field of 0.5 T. The effective magnetic moments were calculated by the equation $\mu_{eff}(T) = 2.84(\chi T)^{1/2}$, where χ is the paramagnetic molar susceptibility corrected for the diamagnetic contribution.

X-ray diffraction study of compounds 9 and 10. X-ray diffraction data sets for single crystals of **9** and **10** were collected on a Bruker AXS Smart Apex diffractometer at 293(2) K. The structures were solved by direct methods and refined by the full-matrix least-squares method with the use of the SHELXTL program package.[18] The hydrogen atoms were located from difference electron density maps and refined isotropically together with nonhydrogen atoms. The crystallographic characteristics and details of X-ray diffraction study for complexes **9** and **10** are given in Table 4.

The crystallographic data for complexes **9**·C_6H_{14} (CCDC 281166) and **10** (CCDC 281165) were deposited with the Cambridge Crystallographic Data Centre.*

Synthesis of complexes. Complexes **1**, **2**, and **3** were synthesized according to a procedure described earlier.[8] The thallium derivatives Tl(ISQ-Me) (**5**) and Tl(ISQ-Pr^i) (**6**) of *o*-iminobenzoquinones were synthesized according to a known procedure.[3]

Bis-[4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinone]chlorocobalt(III), Co(ISQ-Pr^i)$_2$Cl (4). A solution of 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (0.76 g, 2 mmol) in THF (30 mL) was added to a solution of anhydrous cobalt(II) chloride (0.13 g, 1 mmol) in THF (15 mL), and the reaction mixture was stored for 3 days. The solution turned dark-blue. After 3 days, THF was substituted for methanol (20 mL). Then the solution was cooled to 0 °C and stored at this temperature for 5 days. The precipitate that formed was separated by filtration, washed with cold methanol, and dried *in vacuo*. The yield was 0.51 g (59.7%). Found (%): C, 74.00; H, 9.12; Co, 6.71; Cl, 4.03. $C_{52}H_{74}CoClN_2O_2$. Calculated (%): C, 73.17; H, 8.74; Co, 6.90; Cl, 4.15. IR (Nujol mulls), ν/cm^{-1}: 1590 w, 1525 m, 1465 s, 1400 w, 1365 s, 1340 w, 1310 m, 1270 m, 1260 m, 1245 m, 1205 w, 1170 m, 1105 m, 1095 m, 1060 w, 1035 w, 1025 m, 1005 w, 940 w, 915 m, 895 w, 865 m, 830 w, 805 m, 785 m, 775 w, 665 w, 655 w, 585 w, 540 w, 520 w.

Bis-[4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzosemiquinone]rhodanocobalt(III), Co(ISQ-Me)$_2$(SCN) (7). A solution of the Co(ISQ-Me)$_2$Cl complex (**3**) (0.3 g, 0.4 mmol) in THF (15 mL) was heated with stirring in a mixture with a solution of KSCN (0.2 g, 2.06 mmol) in methanol (15 mL) for 8 h. Then the solvent was substituted for hexane and filtered off from the precipitate of the inorganic salt. The filtrate was concentrated and stored at 0 °C for 3 days. The precipitate that formed was separated by filtration, washed with cold hexane,

Table 4. Crystallographic data for complexes **9** and **10**

Parameter	Mn(ISQ-Pr^i)$_2$Cl··C_6H_{14} (**9**·C_6H_{14})	Fe(ISQ-Me)$_2$Br (**10**)
Molecular formula	$C_{58}H_{88}MnClN_2O_2$	$C_{44}H_{58}FeBrN_2O_2$
Molecular weight	935.69	782.68
T/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell parameters		
a/Å	16.213(3)	12.8913(18)
b/Å	20.697(4)	13.4929(19)
c/Å	17.237(3)	14.175(2)
α/deg	90	107.188(2)
β/deg	90.214(4)	109.825(2)
γ/deg	90	90.623(3)
V/Å	5784(2)	2198.9(5)
Z	4	2
d_{calc}/g cm^{-3}	1.074	1.182
M(Mo-Kα)/mm^{-1}	0.313	1.286
$2\theta_{max}$/deg	46.7	59.1
Number of measured reflections	24523	25607
Number of independent reflections	8314	11061
R_{int}	0.0832	0.1062
Number of parameters in refinement	874	684
R factor based on reflections with $I > 2\sigma_I$		
R_1	0.0496	0.0544,
wR_2	0.1013	0.0989
R factor based on all I_{hkl}		
R_1	0.0985	0.1376,
wR_2	0.1160	0.1206
GOOF on F^2	0.826	0.777
Residual electron density (max/min), e A^{-3}	0.256/−0.257	0.520/−0.325

Note. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = R(wF^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$; $S = \text{GOOF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of I_{hkl} and p is the number of parameters in the refinement.

* These data can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre (CCDC): 12 Union Road, Cambridge CD2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk.

and dried *in vacuo*. The yield was 0.18 g (58.9%). Found (%): C, 70.74; H, 7.61; Co, 7.52; S, 4.41. $C_{45}H_{58}CoN_3O_2S$. Calculated (%): C, 70.75; H, 7.65; Co, 7.71; S, 4.20. IR (Nujol mulls), ν/cm^{-1}: 2130 v.s, 2080 v.s, 2065 v.s, 1595 w, 1535 m, 1470 s, 1450 s, 1400 w, 1365 s, 1340 w, 1315 s, 1270 s, 1255 s, 1230 w, 1215 m, 1175 m, 1100 m, 1095 w, 1030 m, 915 m, 900 w, 860 w, 785 w, 770 w, 765 s, 735 w, 655 m, 555 w, 535 w, 520 w, 505 w, 490 w.

Bis-[4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzosemiquinone]iodocobalt(III), Co(ISQ-Me)$_2$I (8). A solution of I_2 (0.30 g, 1.2 mmol) in toluene (20 mL) was added with continuous stirring to a solution of the Co(ISQ-Me)$_2$ complex (**2**) (0.70 g, 1 mmol) in toluene (30 mL). The reaction mixture was stirred for 1 h, concentrated to one-half of the initial volume, and stored at 0 °C for 3 days. The precipitate that formed was filtered off, washed with cold toluene, and dried *in vacuo*. The yield was 0.61 g (73.2%). Found (%): C, 63.53; H, 6.80; Co, 6.73; I, 15.11. $C_{44}H_{58}CoIN_2O_2$. Calculated (%): C, 63.46; H, 7.02; Co, 7.07; I, 15.24. IR (Nujol mulls), ν/cm^{-1}: 1590 w, 1525 m, 1475 s, 1425 s, 1415 w, 1365 s, 1340 w, 1310 w, 1270 s, 1255 s, 1245 w, 1210 m, 1175 s, 1105 m, 1030 w, 1005 m, 915 m, 900 w, 890 w, 862 m, 785 w, 770 s, 660 w, 535 w, 525 w, 505 w.

Bis-[4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinone]chloromanganese(III), Mn(ISQ-Pr^i)$_2$Cl (9). A solution of 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone IBQ-Pr^i (0.38 g, 1 mmol) in THF (10 mL) was added to a solution of anhydrous manganese(II) chloride (0.126 g, 1 mmol) in THF (30 mL). Then a solution of thallium *o*-iminobenzosemiquinolate Tl(ISQ-Pr^i) (**7**), which was prepared from IBQ-Pr^i (0.38 g, 1 mmol) and thallium amalgam,[3] was added to the reaction mixture with continuous stirring. The color of the solution changed to dark-green, and a grayish-white precipitate of TlCl simultaneously formed. The reaction mixture was filtered, THF was removed, the precipitate was dissolved in hexane, and the solution was again filtered. The filtrate was concentrated to one-half of the initial volume and stored at 0 °C for 5 days. The crystalline precipitate of **9**·C_6H_{14} that formed was filtered off and dried *in vacuo*. The yield was 0.69 g (73.7%). Found (%): C, 74.35; H, 9.06; Mn, 6.80; Cl, 3.27. $C_{58}H_{88}MnClN_3O_2$. Calculated (%): C, 74.45; H, 9.48; Mn, 5.87; Cl, 3.79. IR (Nujol mulls), ν/cm^{-1}: 1590 w, 1535 w, 1465 s, 1445 s, 1400 m, 1370 s, 1320 w, 1315 m, 1260 s, 1245 w, 1205 w, 1170 m, 1110 m, 1060 w, 1035 w, 1025 w, 1000 w, 940 w, 915 m, 890 w, 865 m, 830 w, 805 m, 770 w, 730 s, 715 w, 695 w, 655 w, 585 w, 545 m, 465 w.

Bis-[4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzosemiquinone]bromoiron(III), Fe(ISQ-Me)$_2$Br (10) was prepared analogously to **9** from anhydrous $FeBr_2$ (0.216 g, 1 mmol). The yield was 0.535 g (68.4%). IR (Nujol mulls), ν/cm^{-1}: 1580 w, 1525 w, 1465 s, 1415 s, 1365 s, 1335 m, 1320 w, 1250 s, 1200 w, 1175 m, 1100 m, 1030 w, 990 m, 910 w, 875 m, 865 w, 825 w, 780 w, 735 w, 720 w, 660 w, 650 w, 630 w, 600 w, 535 w, 500 w, 480 w.

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References

1. C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
2. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219—221**, 415.
3. A. I. Poddel´skii, G. A. Abakumov, M. P. Bubnov, V. K. Cherkasov, and L. G. Abakumova, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1142 [*Russ. Chem. Bull.*, 2004, **53**, 1189 (Engl. Transl.)].
4. A. I. Poddel´sky, V. K. Cherkasov, M. P. Bubnov, L. G. Abakumova, and G. A. Abakumov, *J. Organomet. Chem.*, 2005, **690**, 145.
5. P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213.
6. H. Chun, C. N. Verani, E. Bothe, P. Chaudhuri, E. Bill, T. Weyhermüller, and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157.
7. H. Chun, P. Chaudhuri, T. Weyhermüller, and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 790.
8. A. I. Poddel´sky, V. K. Cherkasov, G. K. Fukin, M. P. Bubnov, L. G. Abakumova, and G. A. Abakumov, *Inorg. Chim. Acta*, 2004, **357**, 3632.
9. G. A. Abakumov, A. I. Poddel´sky, M. P. Bubnov, G. K. Fukin, L. G. Abakumova, V. N. Ikorskii, and V. K. Cherkasov, *Inorg. Chim. Acta*, 2005, **358**, 3829.
10. G. A. Abakumov, V. K. Cherkasov, A. I. Poddel´skii, M. P. Bubnov, L. G. Abakumova, and G. K. Fukin, *Dokl. Akad. Nauk*, 2004, **399**, 62 [*Dokl. Chem.*, 2004, **399**, 207 (Engl. Transl.)].
11. D. Herebian, P. Ghosh, H. Chun, E. Bothe, T. Weyhermüller, and K. Wieghardt, *Eur. J. Inorg. Chem.*, 2002, 1957.
12. H. Chun, T. Weyhermüller, E. Bill, and K. Wieghardt, *Angew. Chem.*, 2001, **113**, 2552.
13. X. Sun, H. Chun, K. Hildenbrand, E. Bothe, T. Weyhermüller, F. Neese, and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4295.
14. C. S. Batsanov, *Zh. Neorg. Khim.,* 1991, **36**, 3015 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
15. G. A. Abakumov, V. K. Cherkasov, M. P. Bubnov, O. G. Ellert, Yu. V. Rakitin, L. N. Zakharov, Yu. T. Struchkov, and Yu. N. Saf´yanov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2315 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1813 (Engl. Transl.)].
16. Arnold J. Gordon and Richard A. Ford, *The Chemist´s Companion*, A Wiley Interscience Publication, New York, 1972, 541 pp.
17. G. A. Abakumov, N. O. Druzhkov, Yu. A. Kurskii, and A. S. Shavyrin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 682 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 712].
18. G. M. Sheldrick, *Bruker AXS*, Madison, WI, 2000.

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