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3,5-Di-*tert*-butyl-1,4-benzoquinone Ferrocenoylhydrazone and Its Zinc(II), Palladium(II), and Mercury(II) Complexes: Structure and Properties

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Abstract—A new ligand system, 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenoylhydrazone, was synthesized and its complexes with zinc(II), Hg(II), and palladium(II) were prepared. The compounds were studied by IR, electron absorption, and ^{1}H NMR spectroscopy. Structure of the compounds obtained is discussed.

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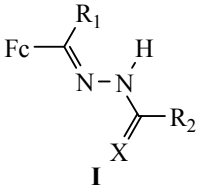
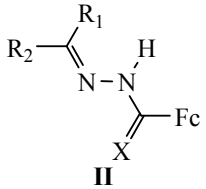
Hydrazones based on the ferrocene derivatives attract attention due primarily to their high complexing ability, as well as in connection with their valuable practical properties, including biological [1–5], photo- and electrochemical activities [6]. These compounds can be divided in two groups: *direct* (**I**) and *reverse* (**II**) hydrazones. The compounds of the first group have been widely studied. This group comprises the products of condensation of an acylferrocene (mono- and diacetylferrocene, formylferrocene, benzoylferrocene) with carboxylic acid hydrazides. The *reverse* hydrazones were obtained by condensation of the carbonyl compounds with ferocenecarboxylic acid hydrazide; they there much less studied.



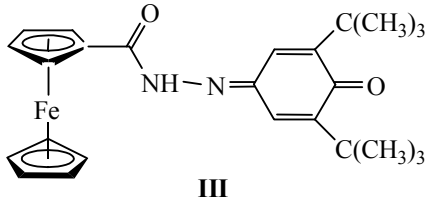
I



II

X = O, S; R_1, R_2 = Alk, Ar, Het; Fc = $C_5H_5FeC_5H_4$.

On the basis of certain *direct* hydrazones a series of coordination compounds of metals has been synthesized and studied [7–15]. It was of interest to extend a number of systems based on *reverse* hydrazones [16–23] using a spatially hindered fragment containing diastereotopic labels, namely 3,5-di-*tert*-butyl-1,4-quinone, as a carbonyl component, to investigate possible dynamic processes caused by the stereochemical nonrigidity of this segment. Such systems are of considerable interest in studying the mechanisms and kinetics of *Z–E* stereodynamics [24, 25] and contribution of various isomeric forms to the structure of the ligands and the complexes based on them. In this regard, we synthesized 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenenoylhydrazone **III** and its complexes with Pd(II), Zn(II), and Hg(II).



III

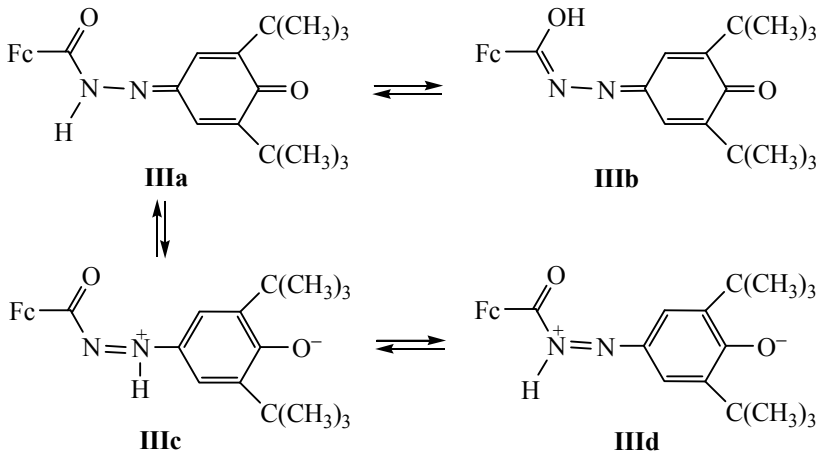
The IR spectrum of 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenenoylhydrazone **III** includes the bands of stretching vibrations of carbonyl groups of the hydrazone (1638 cm^{-1}) and quinone fragments, the hydrazone C=N (1618 cm^{-1}) and NH (3187 cm^{-1}) bonds. The spectrum also contains the bands of torsional vibrations of cyclopentadiene rings at 481 and 500 cm^{-1}.

In order to clarify the ligand structure and to reveal the features of its behavior in solution, we have

recorded its ^{1}H NMR spectra in the solvents of different polarity ($CDCl_3$ and DMSO-d_6) at 25°C.

In the ^{1}H NMR spectrum of the hydrazone in DMSO-d_6 a singlet was registered in a strong field with the chemical shift 1.30 ppm (18H) corresponding to *tert*-butyl groups, a singlet with the chemical shift of 4.16 ppm (5H) corresponding to unsubstituted cyclopentadienyl ring, two signals with the chemical shifts of 4.45 and 6.5 ppm (2H each) corresponding to the pairs of equivalent groups of protons of the substituted cyclopentadienyl ring. In contrast to the *tert*-butyl groups, the quinone *ortho*-protons show magnetic nonequivalence and are registered with different chemical shifts: 6.96 ppm (1H) and 7.64 ppm (1H). The spectrum includes a signal with chemical shift 11.80 ppm corresponding to the imine proton, which disappeares at adding D_2O to the sample.

Given the well-known tautomeric equilibria of the quinone and hydrazone derivatives, the possible tautomers of compound **III** in solution (without accounting for the rotational isomers arising at the rotation of acylferrocene moiety around the C–N bond) are azoquinone ketamine **IIIa**, azoquinone enimine **IIIb**, and two zwitterionic forms, **IIIc** and **IIId**.



IIIa **IIIb** **IIIc** **IIId**

It is known that the spin-spin coupling constant ^4J of the classical aromatic protons is ~1.6 Hz and for the quinoid structures, ~2.2 Hz [24]. In the spectrum of quinine **III** one of the signals of aromatic protons is split into a doublet with spin-spin coupling constant 2.23 Hz, which allows to exclude from consideration the tautomeric forms **IIIc** and **IIId**, the benzoid forms of the quinone.

A feature of the spectrum is the apparent equivalence of *tert*-butyl groups, with the obvious non-equivalence of the aromatic protons. To remove this contradiction we recorded spectrum of this compound in a less polar solvent. In the high-field part of this spectrum were registered two signals of equal intensity (9H) corresponding to *tert*-butyl groups, with chemical shifts 1.33 and 1.38 ppm.

Changing the solvent leads to an additional modification of the spectrum: the signals are shifted, particularly those of the quinone protons, which are shifted relative to each other by 0.15 ppm in $CDCl_3$ and by 0.68 ppm in DMSO-d_6.

The signal of NH proton also is shifted to the strong field and broadened. The signals of the ferrocene moiety underwent minor downfield shifts (~0.15 ppm).

Electron absorption spectrum of the hydrazone **III** contains four absorption bands with the maxima at 205, 290, 360, and 421 nm. The bands positions depend only slightly on the solution pH, in contrast to the molar extinction coefficient of these bands. The greatest dependence on pH showed the bands at the maximum and minimum wavelengths (λ). The most short-wavelength of these bands (λ 205 nm) apparently belongs to the π–π* transitions in the aromatic cyclopentadienyl ligands, and the long-wavelength band corresponds to the *d*–π* transitions in ferrocene [19]. A twofold opposite change in molar extinction coefficients of these bands (see the table) can be attributed to the protonation of the ferrocene fragment.

It is known that, depending on the solution pH, the proton (H^+) is localized either at the iron atom (in strong acid media) or on the π-system of cyclopentadiene ring (in weakly acidic solutions) [26].

The absorption band with the maximum at 360 nm in a weakly alkaline medium undergoes a slight blue shift (by 15 nm) and 1.5-fold drop in intensity due to partial ionization of the ligand.

The presence of several donor centers in the system, connected with a system of conjugated bonds and a labile hydrogen atom, suggests to use it as a ligand for the formation of complexes. At the interaction of the hydrazone with the ions Pd^{2+}, Zn^{2+}, and Hg^{2+} complexes were synthesized of the type **IV**, **V** and **VI**, respectively, with the composition corresponding to the general formula ML_2. The choice of the diamagnetic metals is due to the possibility of studying such complexes by NMR spectroscopy. This ligand forms also complexes with other metals, in particular, with cadmium(II), lead(II), and nickel (II), but chemically pure complexes were obtained only with zinc(II), palladium(II), and mercury(II).

In the ^1H NMR spectrum of the palladium(II) complex in $CDCl_3$ compared to that of the original ligand the strong-field signal of the acidic proton disappears, which confirms the enolization and deprotonation of the compound at the complex formation. Also a significant downfield shift was detected of the signals of the quinone fragment protons, while their nonequivalence was retained. The values of the shift are 0.57 and 1.02 ppm, consistently with the involvement of the quinoneimine nitrogen atom in the coordination. The signals of *ortho*-protons of the cyclopentadiene ring are shifted upfield by 0.27 ppm. The signals of the quinone protons are split into doublets with a spin-spin coupling constant ^4J = 2.6 Hz, characteristic of the coupling of *meta*-protons

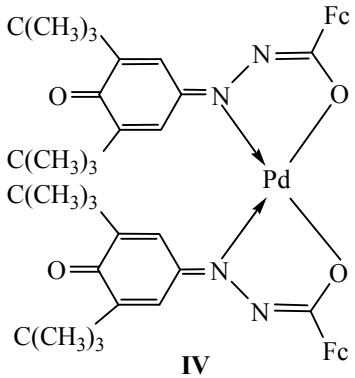
Dependence of parameters of electronic spectrum of 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenoylhydrazone on pH of solution (methanol, c 10^{-5} M)

Absorption band	λ, nm			ε, l mol^{-1} cm^{-1}		
	pH < 7	pH = 7	pH > 7	pH < 7	pH = 7	pH > 7
1	220	205	210	34840	19720	18160
2	295	290	295	11470	13260	11520
3	355	360	345	14340	14570	9870
4	427	421	435	~4000	8500	8300

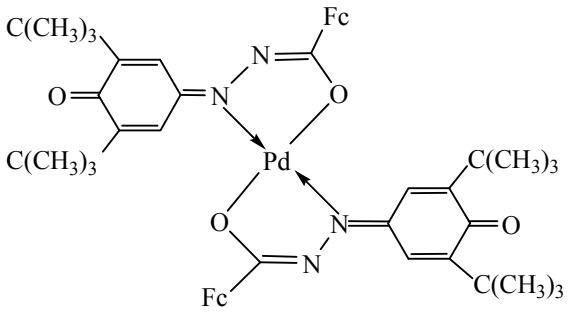
in the quinoid structures. The form of the signals of *tert*-butyl substituents indicates nonequivalence of these groups. It is known that complexes based on sterically hindered quinone azomethines are conformationally labile owing to the *Z–E* isomerization [24, 25]. The same is possible theoretically in the case of the discussed complexes. There are two possible mechanisms of conformational transformation: rotation (requiring high energy expenditure) and planar inversion (energetically less costly).

Such processes are temperature-dependent, which is expressed by the shape of signals in the NMR spectra of respective compounds. At increase in temperature coalescence is observed with degenerating into a singlet of the signals of *tert*-butyl groups.

Since for palladium is typical mainly a planar structure of the chelate site, one can persume equilibrium of *cis*- and *trans*-forms of the complex in solution.



IV
cis-Form



IV
trans-Form

These structures are equally probable, since the intensity ratio of the components in the split signal of *tert*-butyl groups in the spectra corresponds to the ratio of 1:1. However, in the undistorted *cis*-structure of the complex **IV** a significant steric interaction of *tert*-butyl groups is possible. In this connection it should be

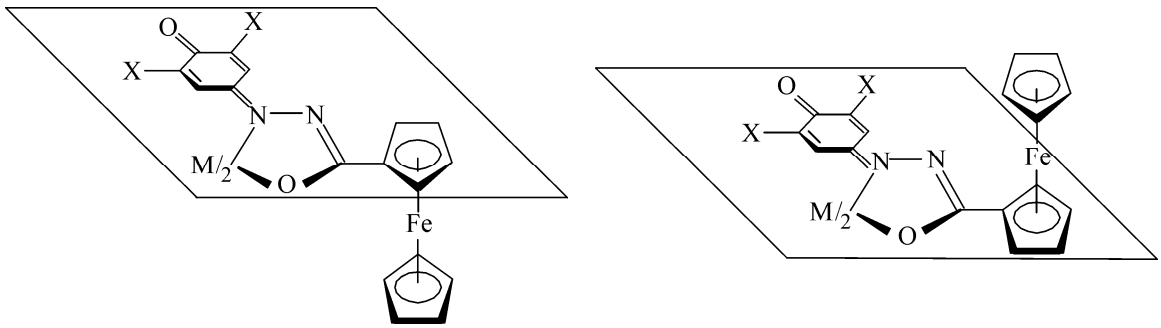


Fig. 1. Enantiomers of the square-planar complex based on hydrazone **III.**

noted that the temperature dependence of the signal shapes, as well as splitting (doubling) of the signals of each of the nonequivalent protons in the quinone and ferrocene groups may be associated with the presence of other conformational equilibrium in the solution, connected with the existence of two enantiomers differing by the mode of stabilization of their structures due to π-conjugation in the cyclopentadiene–quinone hydrazone fragment (Fig. 1).

Comparative analysis of the IR spectra of hydrazone **III** and its complexes with zinc(II) and mercury(II) showed that the coordination leads to the disappearance of the absorption bands of stretching vibrations of the carbonyl group of hydrazone fragment and of N–H bond, with the simultaneous low-frequency displacement by 19 cm^{-1} of the ν(C=N) band. This fact indicates the coordination of the hydrazone as a deprotonated enol form, with involvement in coordination of the azomethine nitrogen atom. In the IR spectra of zinc(II) and mercury(II) complexes are registered also the additional absorption bands ν(C=N) at 1589–1612 cm^{-1}. The presence of these bands indicates the nonequivalence of azomethine groups of the hydrazone and quinone fragments.

In the ^{1}H NMR spectrum of the complex of zinc(II) the following signals were registered: a group of proton signals of the ferrocene structure, δ 4.26 ppm (5H), 4.55 ppm (2H), and 4.97 ppm (2H), a broadened signal at δ 4.25 ppm (2H), and a split high-field signal with chemical shifts of the components 1.32 and 1.38 ppm, corresponding to *tert*-butyl groups (Fig. 2). The components of this signal are not equal in intensity, and the signals of the spectrum are broadened, suggesting the existence in the solution of dynamic equilibrium between different forms of the complex. This assumption was evidenced indirectly at the repeated registration of the spectrum using the same solvent but under the other conditions. The spectrum changes with time, and after 120 h the intensities of the components of the signal of *tert*-butyl groups leveled. The broadened signal detected in the initial spectrum at 7.25 ppm transformed into two components with the chemical shifts 7.05 and 7.25 ppm. In addition, the signal of *ortho*-protons of the substituted cyclopentadiene ligand underwent a downfield shift by 0.18 ppm. To confirm the assumption of possible dynamic processes, we registered the spectra of compounds at elevated temperature (only qualitatively). Changing the temperature allowed to note a tendency to coalesce of the proton signals of *tert*-butyl groups

Apparently, the equilibrium in the solution of the complex is associated with a phenomenon of diagonal twist with rupture of the M–L bond, characteristic of tetrahedral complexes of zinc(II), palladium(II), and mercury(II) (Fig. 3) [24].

Similar features were identified for the complexes of mercury(II), which indirectly indicates the similarity of structures of the zinc(II) and mercury(II) chelates.

In the electron absorption spectra of these complexes in acetone solution a charge transfer band was recorded, which for the zinc(II) complex was found at a shorter wavelength, λ_{max} = 545 nm, and for the palladium(II) complex λ_{max} = 605 nm, which indicates a greater transfer of electron density from the metal to ligand.

EXPERIMENTAL

IR spectra of the samples prepared as suspensions in mineral oil and the fluorinated hydrocarbon oil were obtained on a Varian Scimitar 1000 FT-IR spectrometer in the range of 4000–400 cm^{-1}. ^{1}H NMR

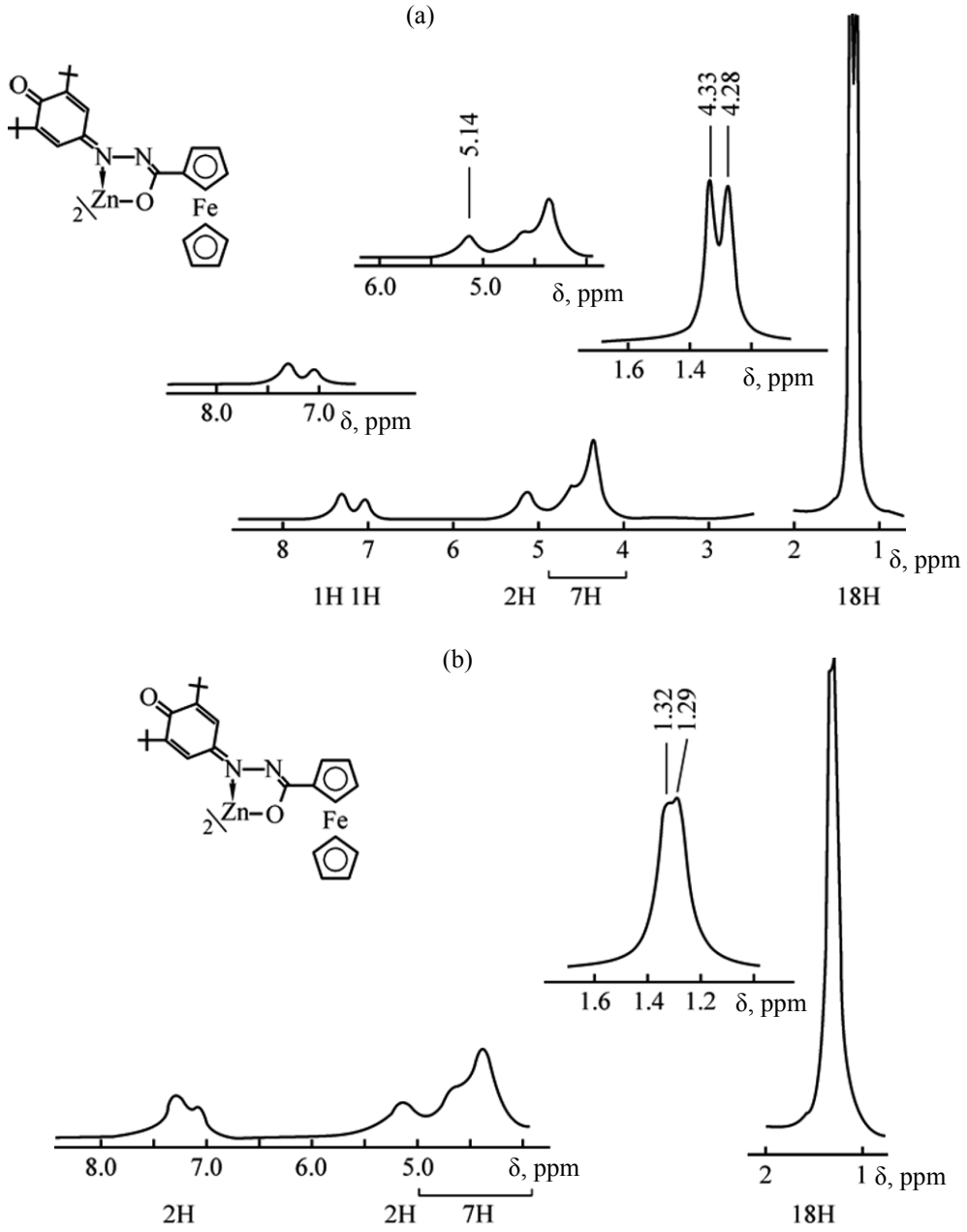


Fig. 2. Changes with temperature in the 1H NMR spectrum of the zinc(II) complex with hydrazide **III.** (a) 293 K and (b) 313 K.

spectra were recorded on a Bruker AM-300 instrument with internal reference TMS. Optical absorption spectra were recorded on a Unicam Helios Gamma spectrometer in cells 1 cm thick in the range of 195–1100 nm, the samples were solutions in methanol or acetone (c 10^{-5} M).

3,5-Di-*tert*-butyl-1,4-benzoquinone ferrocenoylhydrazone (III). To a solution of 0.002 mol of ferrocenecarboxylic acid hydrazide [27] in 10 ml of ethanol was added a solution of 0.002 mol of 3,5-di-*tert*-butyl-1,4-benzoquinone in 3 ml of ethanol. To the reaction mixture was added 2 drops of acetic acid, and the resulting solution was refluxed for 3 h. The solution becomes dark brown. On the next day after cooling a brown precipitate separated and was filtered off and washed twice with ethanol. To purify the hydrazone, it was boiled in a mixture of ethanol and DMF (4 ml of ethanol + 3 ml of DMF) for 1 h. After one day the precipitate was filtered off and again

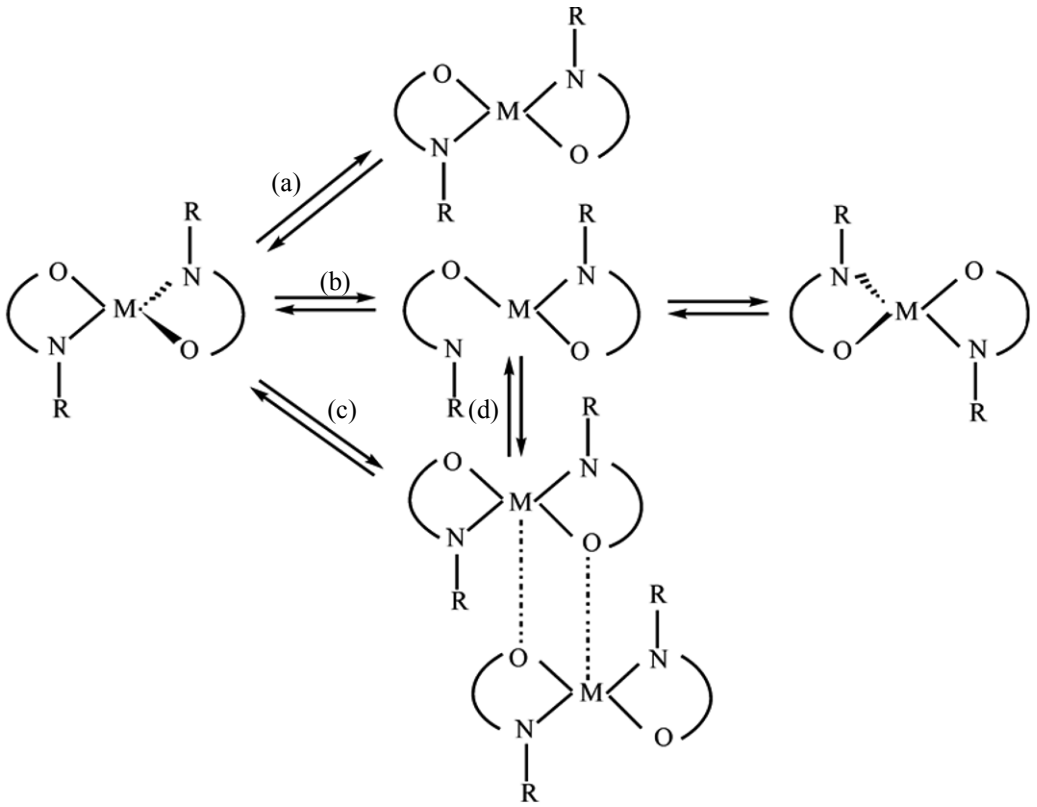


Fig. 3. The possible mechanisms of enantiomerization of tetrahedral structures of complex compounds. (a) intramolecular rearrangement though diagonal twist, (b) intramolecular enantiomerization through cleavage of the M–L bond, (c) or (b–d) degenerate ligand exchange.

boiled in 4 ml of methanol. The product was separated, washed with methanol, and dried in a vacuum at 90°C. Yield 45%, mp 212–213°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.30 s [18H, $C(CH_3)_3$], 4.16 s (5H, C_5H_5) 4.45 s (2H, *ortho*-C_5H_4) , 5.06 s (2H, *meta*-C_5H_4) 6.96 s (1H, quinone), 7.64 s (1H, quinone), 11.80 s (1H, NH). Found, %: C 67.89, H 6.21; N 5.88; Fe 11.96. $C_{25}H_{30}Fe\ N_2O_2$. Calculated, %: C 67.26, H 6.73; N 6.28; Fe 12.56.

Complex of zinc (II) with 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenoylhydrazone. To the boiling suspension of 0.1 g of the hydrazone **III** in 10 ml of anhydrous methanol was added a hot solution of zinc acetate in 3 ml of methanol, the ligand to metal ratio was 2:1. Complete dissolution of the components occurred and formation of a dark-brown solution. The solution was refluxed for 3 h and evaporated to half volume, then left for 48 h. The separated precipitate was isolated and washed twice with a small amount of ethanol. Yield 55%, mp 185–190°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.28 s [9H, $C(CH_3)_3$], 1.32 s [9H, $C(CH_3)_3$], 4.26 br.s (5H, C_5H_5), 4.55 br.s (2H, *ortho*-C_5H_4), 5.14 br.s (2H, *meta*-C_5H_4), 7.25 br.s (2H, quinone). Found, %: C 63.51, H 6.34; N 6.12; Fe 12.07. $C_{50}H_{58}Fe_2N_4O_4Zn$. Calculated, %: C 63.22, H 6.11; N 5.90; Fe 11.80.

Complex of mercury(II) with hydrazone (III) was prepared similarly. A fine crystalline dark-green powder. Yield 32%, mp > 200°C. Found, %: C 55.54, H 5.35; N 4.34; Fe 10.71. $C_{50}H_{58}\ Fe_2HgN_4O_4$. Calculated, %: C 55.30, H 5.35; N 4.61; Fe 10.32.

Complex of palladium (II) with 3,5-di-*tert*-butyl-1,4-benzoquinone ferrocenoylhydrazone was prepared by the similar method, save that palladium acetate was dissolved in acetone. The complex precipitated after 5 min boiling the solution. Yield 67%, mp > 250°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.38 s [9H, $C(CH_3)_3$], 1.39 s [9H, $C(CH_3)_3$], 4.22 s (5H, C_5H_5), 4.45 t (2H, *ortho*-C_5H_4, ^3J 1.9), 4.83 t (2H, *meta*-C_5H_4, ^3J 1.9), 7.68 d (^{1}H, quinone, ^4J 2.9), 8.28 d (^{1}H, quinone, ^4J 2.9). Found, %: C 60.65, H 5.32; N 5.89; Fe 10.89. $C_{50}H_{58}Fe_2N_4O_4Pd$. Calculated, %: C 60.24, H 5.82; N 5.62; Fe 11.24.

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