INTRODUCTION

Hydrazones of polyfunctional carbonyl compounds are among the most studied types of ligand systems in modern coordination and supramolecular chemistry [1–5]. Among compounds of this type, hydrazones containing the ferrocene fragment are of a special interest, because some of them exhibit nonlinear optical properties of the second order [6–8] or biological activity [9, 10]. Numerous complexes based on hydrazones of the carbonyl ferrocene derivatives were described [11–19], whereas ferrocenoylhydrazones of carbonyl compounds are studied to a significantly lower extent [20–26]. In particular, none of ferrocenoylhydrazones and their complexes was studied by X-ray diffraction analysis. The X-ray diffraction results for 2-N-tosylaminobenzaldehyde ferrocenoylhydrazone (H₂L) and the nickel(II) complex based on H₂L (I) are presented.

EXPERIMENTAL

Ferrocenecarboxylic acid hydrazide and 2-N-tosylaminobenzaldehyde obtained by described procedures [26, 27] were used for the synthesis of H₂L.

Synthesis of H₂L. A hot solution of ferrocenecarboxylic acid hydrazide (2 mmol) in ethanol (10 mL) was poured to a hot solution of 2-N-tosylaminobenzaldehyde (2 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 4 h and left to stay overnight. A precipitate was filtered off, washed with ethanol, and dried in vacuo. The product was recrystallized from an ethanol–dimethylformamide (1 : 1) mixture. The yield was 0.50 g (50%); mp > 250°C.

For C₂₅H₂₃N₃O₃SF₇
analy. calcd., %: C, 59.9; H, 4.62; N, 8.38.
Found, %: C, 60.3; H, 4.49; N, 8.61.

IR, ν, cm⁻¹: 3400, 3209 ν(NH), 1637 ν(C=O), 1608 ν(C=N), 1167 νₛ(SO₂), 1091 νᵢ(SO₂), 515, 496 π(Cp–Fe). ¹H NMR (DMSO-d₆), δ, ppm: 11.42 s (1H, NH), 11.16 s (1H, NH), 8.46 s (1H, CH=N), 7.65 s (2H, J = 7.8 Hz, CH₆), 7.55 s (2H, J = 6.9 Hz, CH₆), 7.30 s (2H, J = 7.8 Hz, CH₆), 7.16 m (2H, CH₆), 4.98 s (2H, CH₆), 4.50 s (2H, CH₆), 4.24 s (5H, CH₃), 2.30 s (3H, CH₃).

Synthesis of I. A hot solution of nickel(II) acetate (0.5 mmol) in methanol (10 mL) was poured to a hot solution of H₂L (1 mmol) in methanol (10 mL). The reaction mixture was refluxed for 1 h. A precipitate was filtered off, washed with methanol, dried in vacuo, and recrystallized from methanol. The yield was 0.17 g (30%); mp > 250°C.
2-N-TOSYLAMINOBENZALDEHYDE FERROCENOYLHYDRAZONE

IR, $\nu$, cm$^{-1}$: 3320 $\nu$(OH), 3193 $\nu$(NH), 1608 $\nu$(C=O), 1598 $\nu$(C=N), 1128 $\nu_{as}$(SO$_2$), 1086 $\nu_s$(SO$_2$), 508, 496 $\pi$(Cp–Fe). $\mu$$_{eff}$ 2.94 $\mu_B$ (298 K), 2.91 $\mu_B$ (77.4 K).

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in the range 400–4000 cm$^{-1}$. The samples were prepared as suspensions in Nujol. $^1$H NMR spectra were detected in DMSO-$d_6$ in a Varian Unity 300 spectrometer (300 MHz) in the Fourier impulse mode. Elemental analyses were carried out on a PerkinElmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University. The magnetic susceptibility was determined by the relative Faraday method in the temperature range from 77.4 to 298 K.

X-ray diffraction analyses of compounds H$_2$L and I were carried out on a Bruker APEX II diffractometer (MoK$_\alpha$, $\lambda = 0.71073$ Å, graphite monochromator) at 150(2) K. The initial array of measured intensities was processed using the SAINT [28] and SADABS programs [29]. The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for $F^2_{hk0}$. Hydrogen atoms were placed in the geometrically calculated positions and refined by the riding model ($U_{iso}$(H) = $nU_{iso}$(C), where $n = 1.5$ for the carbon atoms of the methyl groups, and $n = 1.2$ for other C atoms). All calculations were performed using the SHELXTL program package [30]. The PLATON program was used for the analysis of the molecular and crystal structures [31]. The experimental characteristics of the crystallographic data for compounds H$_2$L and I are presented in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CCDC 981876 (H$_2$L) and 981877 (I); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

2-N-Tosylaminobenzaldehyde ferrocenoylhydrazone H$_2$L was synthesized by the condensation of 2-N-tosylaminobenzaldehyde with ferrocenecarboxylic acid hydrazide in ethanol. A single crystal of H$_2$L was obtained by the slow crystallization from a dimethylformamide solution. The single crystal contains two independent molecules (A and B) with similar

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For C$_{51}$H$_{47}$N$_6$O$_7$S$_2$Fe$_2$Ni
anal. calcd., %: C, 56.2; H, 4.34; N, 7.71.
Found, %: C, 56.5; H, 4.45; N, 7.92.

Fig. 1. Structures of two (A, B) independent H$_2$L molecules in the representation of atoms by thermal shift ellipsoids with 50% probability.