

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF NEW
(*Z*)-2-((*E*)-3-(4-NITROPHENYL)-1-FERROCENYLALLYLIDENE)HYDRAZINE CARBOTHIOAMIDE

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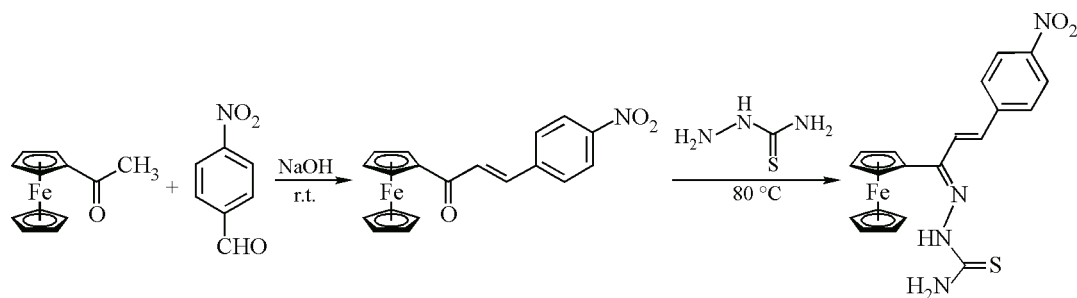
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A new compound of (*Z*)-2-((*E*)-3-(4-nitrophenyl)-1-ferrocenylallylidene)hydrazine carbothioamide is synthesized and its crystal structure is determined by single crystal X-ray diffraction. The compound belongs to the monoclinic $P2_1/n$ space group with the cell parameters: $a = 7.6469(6) \text{ \AA}$, $b = 19.6091(16) \text{ \AA}$, $c = 12.6534(10) \text{ \AA}$, $V = 1875.0(3) \text{ \AA}^3$.

Keywords: X-ray diffraction, monoclinic symmetry, carbothioamide, ferrocenyl.

Thiosemicarbazones as a group of thiourea derivatives have attracted considerable pharmaceutical attention [1] during the past years for their antibacterial and cytotoxic activities toward cancer cells [2—4], among which the conjugated N—N—S system exhibits the anticancer activity [5]. Although several thiosemicarbazone derivatives were synthesized and studied for the potential antitumor activities [5, 6], ferrocene containing chalcone thiosemicarbazones have not been investigated. Herein, a new (*Z*)-2-((*E*)-3-(4-nitrophenyl)-1-ferrocenylallylidene)hydrazine carbothioamide compound is synthesized and its crystal structure is revealed.

Experimental. (*Z*)-2-((*E*)-3-(4-nitrophenyl)-1-ferrocenylallylidene)hydrazine carbothioamide is synthesized by the previously reported procedure with minor modifications [6, 7—10], as shown in Scheme 1.

Scheme 1. Synthesis of (*Z*)-2-((*E*)-3-(4-nitrophenyl)-1-ferrocenylallylidene)hydrazine carbothioamide

To a mixed solution of acetylferrocene (1.0 mmol) and 4-nitrobenzaldehyde (1.0 mmol) in ethanol (5.0 ml) 5.0 M NaOH (2.0 ml) was added. This solution was stirred overnight with the formation of precipitates. Crude chalcone was obtained by filtration, then it was recrystallized from ethanol to give pure chalcone with the yield of 80 %. Then, a mixture of chalcone (1.0 mmol) and thiosemicarbazide (1.0 mmol) was dissolved in ethanol (10 ml), followed by the addition of a catalytic amount of acetic acid. This solution was refluxed for 24 h. After concentration, the crude product was

purified by column chromatography (petroleum ether:dichloromethane = 1:1) to give a pure orange product in 71 % yield, which was dissolved in dichloromethane, and petroleum ether drops were added to obtain a mixed solution. This solution was evaporated slowly at room temperature to form the desired single crystal. ^1H NMR (500 Hz, ppm): 11.03 (s, 1H, *NH*), 8.22 (d, 2H, Ar—*H*), 7.58 (d, 1H, alkenyl-*H*); 7.37 (d, 2H, Ar—*H*), 7.02 (s, 2H, *NH*₂), 6.33 (d, 1H, alkenyl-*H*), 4.62—4.57 (m, 4H, Fc—*H*), 4.51 (s, 5H, Fc—*H*); IR (KBr, cm^{-1}): 3485(vs), 3245(vs), 1475(vs), 1510(m), 1150(m), 481(s); Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{FeN}_4\text{O}_2\text{S}$: C, 55.31; H, 4.18; N, 12.90. Found: C, 55.50; H, 4.32; N, 12.85.

NMR, IR, and elemental analysis. FT-IR spectra were recorded in the range 400—4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. ^1H NMR spectrum was recorded in CDCl_3 at 500 MHz on a Bruker Advance 600 spectrometer. Elemental analysis for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer.

X-ray crystallography. The crystallographic data were collected on a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K using the ω -scan technique. The diffraction data were integrated using the SAINT program [11], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [12]. The structures were

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Crystal data and structure refinement for the complex

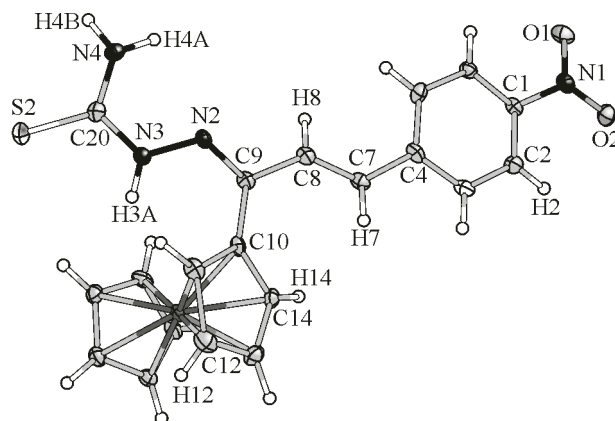
Chemical formula	$\text{C}_{20}\text{H}_{18}\text{FeN}_4\text{O}_2\text{S}$
Molecular weight	434.29
Crystal system	Monoclinic
Space group	$P2_1/n$
$a, b, c, \text{ \AA}$	7.6469(6), 19.6091(16), 12.6534(10)
β , deg.	98.8120(10)
T , K	296(2)
$V, \text{ \AA}^3$	1875.0(3)
Z	4
$D_c, \text{ g/cm}^{-3}$	1.539
$\mu, \text{ mm}^{-1}$	0.940
$F(000)$	896
θ range, deg.	1.93/25.01
Index ranges (h, k, l)	−9/9, −23/23, −12/15
R_{int}	0.0597
Refined data, parameter, restriction	3300, 253, 0
Observed reflections with $I > 2\sigma(I)$	2819
GOOF	1.040
Final R factor [$I > 2\sigma(I)$]	$R_1 = 0.0341, wR_2 = 0.0856$
R factor (all data)	$R_1 = 0.0427, wR_2 = 0.0905$
Large diff. peak and hole, $e/\text{ \AA}^3$	0.690 and −0.428

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o)^2]^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP].$$

$$P = (F_o^2 + 2F_c^2)/3.$$

Fig. 1. Molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level



solved by direct methods and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [13]. Hydrogen atoms were generated geometrically. The details of the crystal parameters are summarized in Table 1.

Results and discussion. Fig. 1 presents the title compound, which was crystallized with a monoclinic crystal system and a $P2_1/n$ space group.

For the ferrocenyl moiety, the distance from Fe(II) to the center of the substituted cyclopentadiene ring (C_{ps}) is 1.381(1) Å, while the distance of the unsubstituted ring (C_p) is 1.382(4) Å. Moreover, the C_{ps} —Fe— C_p bond angle is 175.43(5) Å, which means that central Fe(II) locates almost in the middle of the two cyclopentadiene rings. However, two cyclopentadiene rings are not parallel to each other with a small dihedral angle of 6.08(3) Å.

For the other parts, the N1—O1, N1—O2, C7—C8, C9—N2, and C20—S2 bond lengths are 1.230(3) Å, 1.227(2) Å, 1.320(3) Å, 1.295(3) Å, and 1.682(2) Å respectively, indicating that they are double bonds. Meanwhile, the C20—N4 and N2—N3 bond distances are 1.327(3) Å and 1.370(2) Å, making them single bonds.

While no intramolecular hydrogen bonds are found, three intermolecular hydrogen bonds are revealed to be N4—H4B···O2', C12—H12···O1', and C14—H14···O1'. For N4—H4B···O2', the N4—H4B, H4B···O2' and N4···O2' distances are found to be 0.91 Å, 2.20 Å, and 3.031(3) Å; the bond angle is 152°. As for C12—H12···O1', the bond lengths are 0.98 Å, 2.49 Å, and 3.394(3) Å for C12—H12, H12···O1', and C12···O1', respectively, while the bond angle is 153°. For the third one of C14—H14···O1', the corresponding values are found to be 0.98 Å, 2.57 Å, and 3.323(3) Å for the bond lengths, and 134° for the bond angle. Moreover, the symmetric codes for the above hydrogen bonds are $-1+x, y, -1+z$; $2-x, -y, 2-z$, and $5/2-x, 1/2+y, 3/2-z$ respectively. Furthermore, a weak interaction between S2 and C2'—H2' is also found. This weak interaction together with the N4—H4B···O2' hydrogen bond can form an eight-membered ring, which will further construct a 1D zigzag chain structure with all ferrocenyl groups located at the same side, as depicted in Fig. 2.

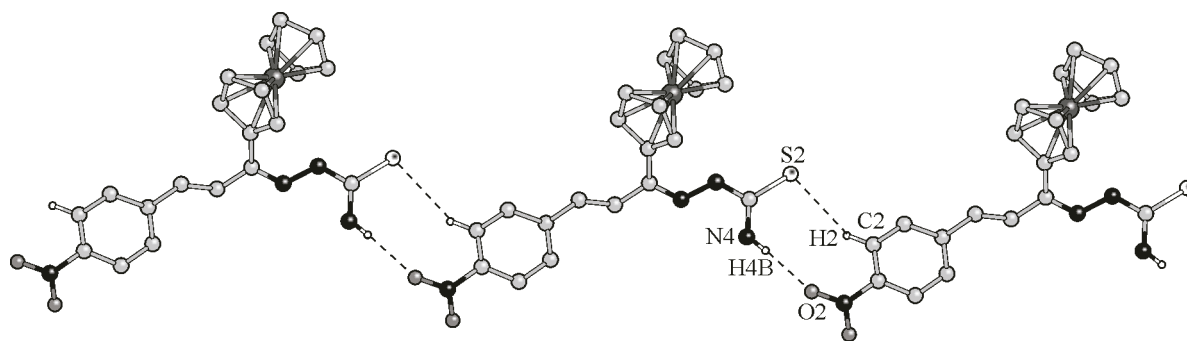


Fig. 2. 1D zigzag chain structure of the title compound

Supplementary material. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 927316, and is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

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