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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF 6-FERROCENYL-3-PHENYL-[1,2,4]TRIAZOLO[3,4-*b*][1,3,4]THIADIAZOLE

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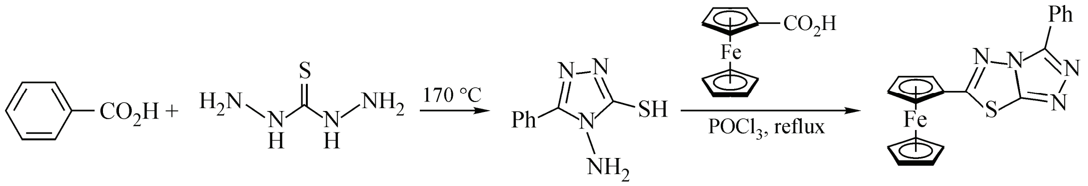
A new compound of 6-ferrocenyl-3-phenyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole is synthesized and its single crystal structure is determined by X-ray diffraction method. The compound belongs to the monoclinic $P2_1/c$ space group with cell parameters: $a = 10.5523(12)$ Å, $b = 13.8414(16)$ Å, $c = 11.4303(13)$ Å, $V = 1603.5(3)$ Å^3.

Keywords: X-ray diffraction, monoclinic symmetry, triazole, thiadiazole, ferrocenyl.

For their wide spectrum applications in biology [1] 1,2,4-triazoles and 1,3,4-thiadiazoles possess diverse types of biological properties, such as antimicrobial [2], antibacterial [3], antitubercular [4], anti-inflammatory [5, 6], and antihypertensive [7] activities, etc. Moreover, triazolothiadiazole can be viewed as a cyclic analogue to two very important components: thiosemicarbazide and biguanide, which often display diverse biological properties. Herein, a new compound of the 1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazole ring system is synthesized and its X-ray crystal structure is revealed.

Experimental. The 6-ferrocenyl-3-phenyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole compound is synthesized by the previously reported procedure with minor modifications [8], as shown in Scheme 1.



Scheme 1. Synthesis of 6-ferrocenyl-3-phenyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole

A mixture of benzoic acid (1 mmol) and thiocarbohydrazide (1 mmol) was warmed up to 170 °C for 1 h. After cooling, water was added into the solution. This solution was acidified by HCl (conc.) to give precipitates, which were filtered and collected to obtain crude 5-benzoic-4-amino-3-merapto-1,2,4-triazole with the yield of 80 %. Then, a mixture of 5-benzoic-4-amino-3-merapto-1,2,4-triazole (1 mmol) and ferrocenecarboxylic acid (1 mmol) in phosphoryl chloride was refluxed for 6 hours. Excess phosphoryl chloride was removed under reduced pressure. The residue was poured into ice water and the mixture was stirred at room temperature for one hour; sodium bicarbonate was added into the solution gradually until the solution was neutral. The precipitated solid was filtered, dried and recrystallized to get the pure product, which was dissolved in methanol, followed by adding petroleum ether to get the mixed solution. This solution was evaporated slowly at room temperature to give the desired single crystal.

Table 1

Crystal data and structure refinement for the complex

Chemical formula	C19H14FeN4S	$F(000)$	792
Molecular weight	386.25	θ range, deg.	2.37 / 28.29
Crystal system	Monoclinic	Index ranges (h, k, l)	–13/14, –18/18, –15/15
Space group	$P2_1/c$	R_{int}	0.0917
a, b, c, Å; β, deg.	10.5523(12), 13.8414(16),	Refined data, parameter, restriction	4006, 226, 0
	11.4303(13); 106.1690(10)	Observed reflections with $I > 2\sigma(I)$	3063
T, K	293(2)	GOOF	0.947
V, Å^3	1603.5(3)	R_1 / wR_2 [$I > 2\sigma(I)$]	0.0344 / 0.0760
Z	4	R_1 (all data)[a]	0.0506
D_c, g·cm^{-3}	1.600	wR_2 (all data)[b]	0.0810
μ, mm^{-1}	1.080	$(\Delta\rho)_{\max}$ / $(\Delta\rho)_{\min}$, e/Å^3	0.530 / –0.408

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[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$;

[b] $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)|/\Sigma|w(F_0)^2|^{1/2}$, where $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$; $P = (F_0^2 + 2F_c^2)/3$.

Table 2

Selected geometric parameters (Å, deg.)

C4—C7	1.466(3)	C5—S2	1.733(2)	N4—C7—N2	108.12(16)	N3—C5—N2	111.74(17)
C7—N4	1.320(2)	C9—S2	1.7683(18)	N4—C7—C4	125.10(17)	N1—C9—S2	117.39(14)
C7—N2	1.375(2)	C9—N1	1.307(2)	N2—C7—C4	126.70(17)	C5—S2—C9	87.51(9)
N3—N4	1.403(2)	N1—N2	1.389(2)	C9—N1—N2	107.07(15)	C5—N2—C7	105.69(15)
C5—N3	1.316(2)	C9—C11	1.449(2)	N1—C9—C11	123.04(17)	N2—C5—S2	109.62(14)
C5—N2	1.364(2)			C7—N4—N3	109.58(15)	C5—N2—N1	118.40(15)
				C5—N3—N4	104.86(16)	C11—C9—S2	119.56(14)

X-ray crystallography. The crystallographic data collections were carried out on a Bruker Smart Apex II CCD area-detector diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 293(2) K using the ω-scan technique. The diffraction data were integrated using the SAINT program [9], which was also used for the intensity corrections for Lorentz and polarization effects. Semiempirical absorption correction was applied using the SADABS program [10]. The structures were 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 [11]. Hydrogen atoms were generated geometrically. Details of crystal parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and discussion. The titled compound crystallized in a monoclinic crystal system with a $P2_1/c$ space group, as depicted in Fig. 1.

For the ferrocenyl moiety, the distance from Fe(II) to the center of the substituted cyclopentadiene ring (C_{ps}) is 1.368(5) Å, while this distance is 1.375(2) Å for the unsubstituted one (C_p). The bond angle of C_{ps}—Fe—C_p is 177.98(8) Å, which means that central Fe(II) is located almost in the middle of the two cyclopentadiene rings. Furthermore, two cyclopentadiene rings are not parallel to each other with a small dihedral angle of 4.64(5) Å.

In the [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole ring, the C7—N4, C5—N3, and C9—N1 bond lengths are 1.320(2) Å, 1.316(2) Å, and 1.307(2) Å respectively, which is consistent with the typical values of C=N double bonds. Meanwhile, the C5—S2 and C9—S2 bond distances are 1.733(2) Å and 1.7683(18) Å, indicating two single bonds.

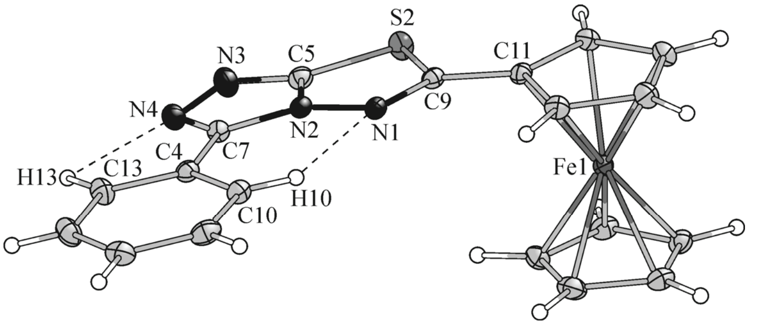

Fig. 1. Molecular structure of the titled compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

Moreover, two weak intramolecular hydrogen bonds were found to be C10—H10···N1 and C13—H13···N4, as depicted in Fig. 1. For C10—H10···N1 the C10—H10, H10···N1, and C10···N1 distances are 0.93 Å, 2.49 Å, and 3.153(3) Å; the bond angle is found to be 120°. As for C13—H13···N4, the corresponding C13—H13, H13···N4, and C13···N4 bond lengths are 0.93 Å, 2.55 Å, and 2.877(3) Å respectively. The C13—H13···N4 bond angle is 101°. Possible $\pi\cdots\pi$ weak interactions between the S2 atom and the adjacent ferrocenyl rings were found to be too weak to be considered.

Supplementary material. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 874161, and is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

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