ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2013. Том 54, № 6 *Ноябрь – декабрь* *С. 1077 – 1081*

UDC 548.73:547.13:546.72

CRYSTAL STRUCTURES OF METHYL AND BENZYL 5-FERROCENYL-3,5-DIMETHYL-2-PYRAZOLINE-1-DITHIOCARBOXYLATE

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Received May, 17, 2012

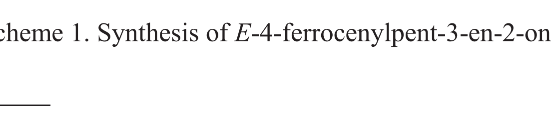
Reactions of *E*-4-ferrocenylpent-3-en-2-one with *S*-methyldithiocarbazate or *S*-benzyldithiocarbazate result in the formation of methyl 5-ferrocenyl-3,5-dimethyl-2-pyrazoline-1-dithiocarboxylate (**1**) or benzyl 5-ferrocenyl-3,5-dimethyl-2-pyrazoline-1-dithiocarboxylate (**2**). The single crystals of both products are obtained and their structures are identified by X-ray diffraction method with triclinic *P*-1 space groups. The cell parameters for compound **1** are as follows: $a = 7.7029(8)$ Å, $b = 10.1631(11)$ Å, $c = 10.7305(12)$ Å, $\alpha = 101.3270(10)°$, $\beta = 90.6740(10)°$, $\gamma = 94.8390(10)°$, and $V = 820.40(15)$ Å^3. For compound **2**, the crystallographic data are: $a = 7.953(3)$ Å, $b = 10.970(5)$ Å, $c = 12.534(3)$ Å, $\alpha = 84.718(5)°$, $\beta = 81.651(3)°$, $\gamma = 76.274(4)°$, and $V = 1049.1(7)$ Å^3.

Keywords: pyrazoline, ferrocenyl, dithiocarboxylate, X-ray.

Pyrazolines were first reported by Knorr and Blank in 1885 [1]. Since then, a large number of pyrazoline derivatives were synthesized due to their wide variety of biological activities such as antidepressant [2], anti-inflammatory [3], antimicrobial [4], antimycobacterial [5], anticancer [6], antibacterial [7], and photoluminiscence activities [8], etc. Besides, pyrazoline derivatives were also used as fluorescent brightening agents for their strong blue fluorescence in solution [9] and high fluorescence quantum yields [10]. While several new methodologies have been applied to the synthesis of pyrazolines and their derivatives [11] recently, we, herein, present the syntheses and the crystal structures of two new pyrazoline derivatives.

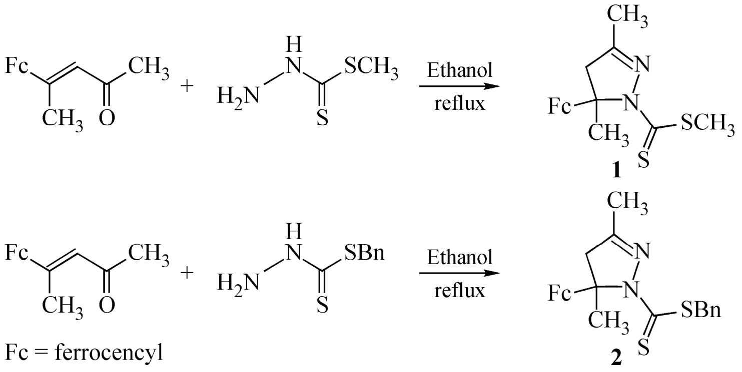
EXPERIMENTAL

Synthesis of *E*-4-ferrocenylpent-3-en-2-one. In a sealed tube, acetylferrocene (5.0 mmol) was dissolved in 20 ml of ethanol, followed by adding 6.0 M NaOH solution (5.0 ml) and acetone (5.0 mmol). This solution was shaken at room temperature for 48 h. The precipitate was collected by filtration to obtain the crude product, which was purified by recrystallization from ethanol, giving a pure orange product with a yield of 75 % (Scheme 1).



Scheme 1. Synthesis of *E*-4-ferrocenylpent-3-en-2-one

Synthesis of compounds 1 and 2. A solution of *E*-4-ferrocenylpent-3-en-2-one (1.0 mmol) and *S*-methyldithiocarbazate (1.0 mmol) or *S*-benzyldithiocarbazate (1.0 mmol) in 10 ml of ethanol was refluxed for 48 hours. This solution was cooled and stored in a freezer at 0 °C for 12 hours with the formation of yellow precipitates. The crude products were collected by filtration and recrystallized from ethanol to give pure products, which were redissolved in dichloromethane and slowly evaporated to obtain the desired crystal (Scheme 2).



Fc = ferrocencyl

Scheme 2. Synthesis of methyl 5-ferrocenyl-3,5-dimethyl-2-pyrazoline-1-dithiocarboxylate (**1**) and benzyl 5-ferrocenyl-3,5-dimethyl-2-pyrazoline-1-dithiocarboxylate (**2**)

X-ray Crystallography. For single crystal X-ray diffraction studies a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) is used at 296(2) K to collect the crystallographic data using the ω-scan technique. The diffraction data were integrated using the SAINT program [12], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [13]. 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 [14]. Hydrogen atoms were generated geometrically. Table 1 collects the details of the crystal parameters, while Table 2 and Table 3 give the selected bond lengths and angles for each crystal.

RESULTS AND DISCUSSION

For the single crystals, both compounds crystallized in triclinic crystal systems and *P*-1 space groups, as depicted in Figs. 1 and 2.

For the ferrocenyl moieties, the distances from Fe(II) to the center of the substituted cyclopentadiene ring (C_{ps}) and unsubstituted cyclopentadiene (C_p) are nearly the same, being 1.653(2) Å and 1.658(9) Å for compound **1** and 1.653(3) and 1.654(1) Å for compound **2**. The C_{ps}—Fe—C_p bond angles are 176.53(1)° and 177.35(3)° for each compound. These values indicate that for both compounds, the central Fe(II) atom locates almost in the middle of the two cyclopentadiene rings. Besides, two cyclopentadiene rings are not parallel to each other. Small dihedral angles are found to be 4.63° and 3.44° Å for compounds **1** and **2**.

For the pyrazolinyl rings, C11 is the only stereocenter with four different substituents. The N2—C11—C13 bond angles are 99.57(1)° and 99.5(6)° for corresponding compoundы **1** and **2**, which can be explained by the restriction of the pyrazolinyl rings. All other bond angles are similar to the regular tetrahedral values, ranging from 108.34(2)° to 113.6(7)°, which results in distorted tetrahedral geometries for the C11 stereocenters. The C14=N1 and C11—N2 are typical double and single bonds with the bond lengths being 1.280(2) Å, 1.529(2) Å and 1.274(1) Å, 1.541(9) Å for compounds **1** and **2** re-

Table 1

Crystal data and structure refinement for both compounds

Formula	$C_{17}H_{20}FeN_2S_2$ (**1**)	$C_{23}H_{24}FeN_2S_2$ (**2**)
M_r	372.32	448.41
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a, b, c, Å	7.7029(8), 10.1631(11), 10.7305(12)	7.953(3), 10.970(5), 12.534(3)
α, β, γ, deg.	101.3270(10), 90.6740(10), 94.8390(10)	84.718(5), 81.651(3), 76.274(4)
T, K	296(2)	296(2)
V, Å^3	820.40(15)	1049.1(7)
Z	2	2
ρ_{calc}, g·cm^{-3}	1.507	1.419
μ, mm^{-1}	1.170	0.929
$F(000)$	388	468
θ range, deg.	2.5—27.6	2.6—27.5
Radiation type, λ, Å	MoK_α, 0.71073	MoK_α, 0.71073
Index ranges (h, k, l)	–9/9, –12/12, –13/13	–9/9, –11/13, –15/15
R_{int}	0.0187	0.0301
Parameter refined	3310	4065
Refinement parameters	202	255
Refinement restrictions	0	0
Reflections with $I > 2\sigma(I)$	3037	3286
GOOF	1.130	1.176
Final R factor [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0751$	$R_1 = 0.0803$, $wR_2 = 0.2323$
R factor (all data)	$R_1 = 0.0306$, $wR_2 = 0.0799$	$R_1 = 0.0935$, $wR_2 = 0.2376$
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e/Å^3	0.276 / –0.391	1.334 / –0.515

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

[b] $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)|/\Sigma w(F_o)^2|^{1/2}$, 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.) *for compound* **1**

C11—N2	1.529(2)	C11—C13	1.541(2)	C10—C11	1.508(2)
C13—C14	1.492(2)	C14—N1	1.280(2)	N1—N2	1.408(2)
C16—N2	1.343(2)	C16—S3	1.6607(2)	C16—S4	1.7813(2)
C10—C11—C12	112.81(2)	N2—C11—C12	108.34(2)	C10—C11—C13	112.24(2)
N2—C11—C13	99.57(1)	C14—C13—C11	104.62(1)	N1—C14—C13	114.30(2)
C14—N1—N2	108.64(1)	N1—N2—C11	111.87(1)	C16—N2—N1	117.73(1)
C16—N2—C11	129.16(1)	N2—C16—S3	124.77(1)	S3—C16—S4	123.49(1)

spectively. However, N1—N2 and C16—N2 bonds are slightly shorter with the values of 1.408(2) Å and 1.343(2) Å for compound **1** and 1.418(9) Å and 1.337(1) Å for compound **2**. This is attributed to the conjugation of the sp^2 hybridized N2 atom with C14=N1 and C16=S3 (or C16=S1) double bonds, generating a large conjugated system involving C14, N1, N2, C16, and S3 atoms for compound **1** (or C14, N1, N2, C16, and S1 for compound **2**).

Table 3

Selected geometric parameters (Å, deg.) *for compound* **2**

C11—N2	1.541(9)	C11—C13	1.531(1)	C10—C11	1.511(1)
C13—C14	1.492(1)	C14—N1	1.274(1)	N1—N2	1.418(9)
C16—N2	1.337(1)	C16—S1	1.670(8)	C16—S2	1.763(8)
C10—C11—C12	113.6(7)	N2—C11—C12	111.7(6)	C10—C11—C13	113.2(7)
N2—C11—C13	99.5(6)	C14—C13—C11	104.8(7)	N1—C14—C13	114.9(7)
C14—N1—N2	108.2(7)	N1—N2—C11	111.6(6)	C16—N2—N1	118.0(6)
C16—N2—C11	129.3(7)	N2—C16—S1	123.8(6)	S1—C16—S2	124.1(5)

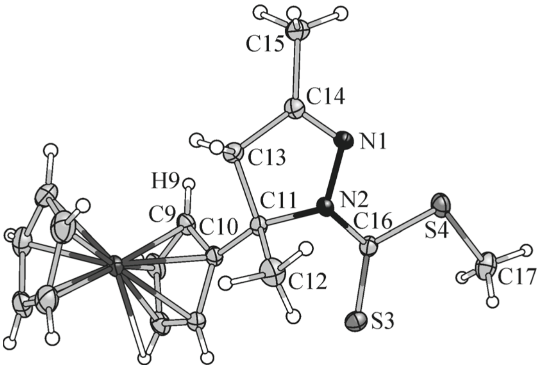

Fig. 1. Molecular structure of compound **1** with the atom numbering scheme.
Displacement ellipsoids are drawn at the 30 % probability level

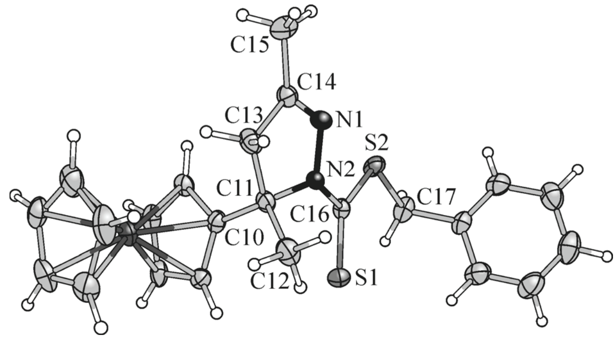

Fig. 2. Molecular structure of compound **2** with the atom numbering scheme.
Displacement ellipsoids are drawn at the 30 % probability level

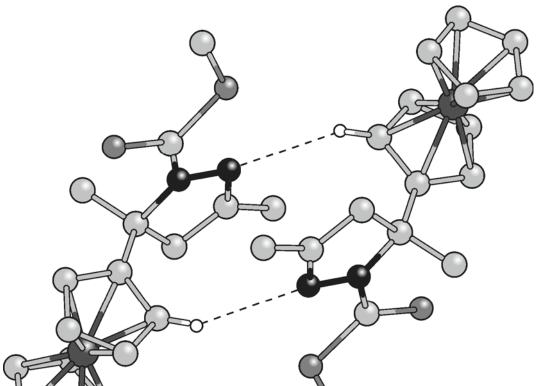

Fig. 3. Bimolecular system of compound **1** *via* the intermolecular C9—H9···N1′ hydrogen bond

Compared with compound **2**, which has no weak interactions, an intermolecular hydrogen bond is revealed in compound **1** as C9—H9···N1′. The C9—H9, N1′···H9, and C9···N1′ bond lengths are 0.930 Å, 2.739(3) Å, and 3.528 Å, while the bond angle is 143.20° for C9—H9···N1′. With this intermolecular hydrogen bond, a bimolecular system can be found, as shown in Fig. 3.

Supplementary material. CIF files containing complete information on the studied structures were deposited with CCDC, deposition numbers 882159 and 882160, and are freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

This work is financially supported by the ″Six Talented Summit″ funding of Jiangsu Province of P. R. China (No. NO2011-JZ-017).

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