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CRYSTAL STRUCTURES OF 2-FERROCENYLMETHYLIDENEHYDRAZONO-1,3-DITHIANE AND 2-FERROCENYLMETHYLIDENEHYDRAZONO-1,3-DITHIEPANE**P. Wu**

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Two compounds of 2-ferrocenylmethylidenehydrazono-1,3-dithiane (**1**) and 2-ferrocenylmethylidenehydrazono-1,3-dithiepane (**2**) are synthesized and their single crystal structures are determined by the X-ray diffraction method. Compound **1** belongs to the orthorhombic $Pca2_1$ space group with the cell parameters: $a = 13.989(4) \text{ \AA}$, $b = 5.785(2) \text{ \AA}$, $c = 18.231(5) \text{ \AA}$, $V = 1475.4(7) \text{ \AA}^3$; while compound **2** crystallizes in a monoclinic symmetry, $P2_1/c$ space group with $a = 15.320(2) \text{ \AA}$, $b = 5.8028(6) \text{ \AA}$, $c = 36.584(4) \text{ \AA}$, $\beta = 91.932(1)^\circ$ and $V = 3250.4(6) \text{ \AA}^3$.

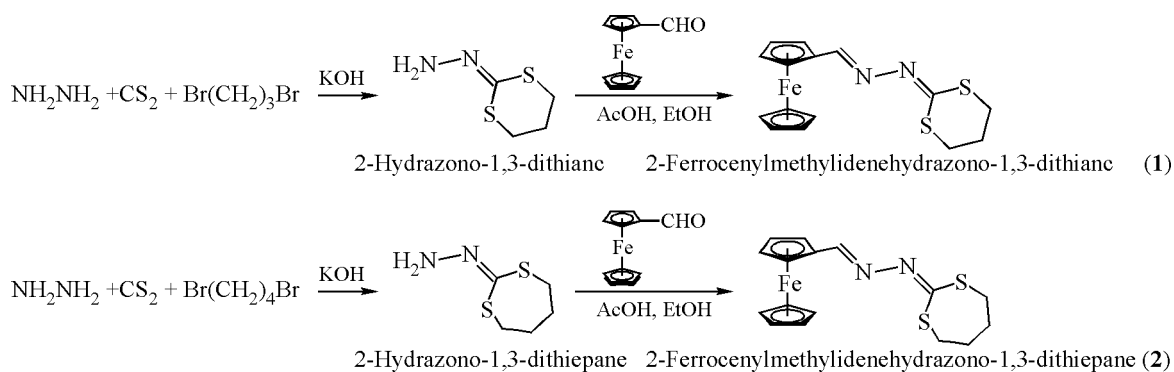
Keywords: X-ray diffraction, dithiane, dithiepane, ferrocenyl.

Ferrocene and its derivatives have attracted vast interest in pharmaceutical, materials and coordination chemistries [1—5]. A ferrocenyl version of tamoxifen was synthesized in 2003, and it can bind to the estrogen binding sites, resulting in a cytotoxicity effect [1—3]. The decomposition of ferrocene into iron nanoparticles allows it to be used as a catalyst for the production of carbon nanotubes [4]. Chiral ferrocenyl phosphines are often employed as ligands for metal-catalyzed reactions: a typical example is 1,1'-bis(diphenylphosphino)ferrocene for Pd-coupling reactions [5]. Besides, 2-hydrazono-1,3-dithiolcycloalkanes are also found to be biologically active compounds. An example for its Schiff base is Yekuline that has biological activities on *E. coli* and streptococcus [6]. Since we have continuous interest in ferrocene chemistry [7], 2-hydrazono-1,3-dithiane and 2-hydrazono-1,3-dithiepane is used to react with ferrocenecarboxaldehyde, giving 2-ferrocenylmethylidenehydrazono-1,3-dithiane and 2-ferrocenylmethylidenehydrazono-1,3-dithiepane respectively. The single crystals of both compounds are obtained and their X-ray crystal structures are revealed.

EXPERIMENTAL

2-hydrazono-1,3-dithiane and 2-hydrazono-1,3-dithiepane are synthesized according to the previously reported methods [8]. The reaction of 2-hydrazono-1,3-dithiane or 2-hydrazono-1,3-dithiepane with ferrocenecarboxaldehyde gives 2-ferrocenylmethylidenehydrazono-1,3-dithiane and 2-ferrocenylmethylidenehydrazono-1,3-dithiepane, as shown below.

To a solution of ferrocenecarboxaldehyde (5.0 mmol) with 2-hydrazono-1,3-dithiane (5.0 mmol) or 2-hydrazono-1,3-dithiepane (5.0 mmol) in 30 ml of ethanol, a few drops of HCl(conc.) were added. This solution was stirred at room temperature overnight before refluxing for 6 h with the formation of precipitates. This solution was concentrated to its half volume and cooled in a freezer overnight. The dark red crude product was obtained by filtration, which was recrystallized from ethanol to give pure orange solids. Dichloromethane was used to dissolve the pure products, which were slowly evaporated



Scheme 1. Synthesis of 2-ferrocenylmethylidenehydrazono-1,3-dithiane (1) and 2-ferrocenylmethylidenehydrazono-1,3-dithiepane (2)

at room temperature to form the desired single crystals solid in whole. Characteristic data for compound **1**: IR (KBr): 3075 cm⁻¹, 1568 cm⁻¹, 1456 cm⁻¹, 1089 cm⁻¹, 1008 cm⁻¹, 900 cm⁻¹; Anal. Calcd. for C₁₅H₁₆FeN₂S₂: C, 52.33; H, 4.68; N, 8.14. Found: C, 52.42; H, 4.65; N, 8.12. For compound **2** IR (KBr): 3080 cm⁻¹, 1589 cm⁻¹, 1469 cm⁻¹, 1102 cm⁻¹, 995 cm⁻¹, 886 cm⁻¹; Anal. Calcd. for C₁₆H₁₈FeN₂S₂: C, 53.63; H, 5.06; N, 7.82. Found: C, 53.70; H, 5.02; N, 7.79.

Table 1

Crystal data and structure refinement for both compounds

	C ₁₅ H ₁₆ FeN ₂ S ₂ (1)	C ₃₂ H ₃₆ Fe ₂ N ₄ S ₄ (2)
Formula	C ₁₅ H ₁₆ FeN ₂ S ₂ (1)	C ₃₂ H ₃₆ Fe ₂ N ₄ S ₄ (2)
<i>M_r</i>	344.27	716.59
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	13.989(4), 5.785(2), 18.231(5)	15.320(2), 5.8028(6), 36.584(4)
α, β, γ, deg.	90, 90, 90	90, 91.932(1), 90
<i>T</i> , K	296(2)	293(2)
<i>V</i> , Å ³	1475.4(7)	3250.4(6)
<i>Z</i>	4	4
ρ _{calc} , g · cm ⁻³	1.550	1.464
μ, mm ⁻¹	1.295	1.179
<i>F</i> (000)	712	1488
θ range, deg.	2.23—25.00	1.76—25.10
Radiation type λ, Å	0.71073	0.71073
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	-16/16, -6/6, -21/21	-18/18, -6/6, -43/39
<i>R</i> _{int}	0.0835	0.0362
Parameter refined	2586	5763
Refinement parameters / restrictions	181 / 1	426 / 12
Reflections with <i>I</i> > 2σ(<i>I</i>)	2229	4620
GOOF	1.032	1.040
Final <i>R</i> factor [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0432, <i>wR</i> ₂ = 0.1083	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.0979
<i>R</i> factor (all data)	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.1144	<i>R</i> ₁ = 0.0561, <i>wR</i> ₂ = 0.1058
Δρ _{max} / Δρ _{min} , e/Å ³	0.447 / -0.335	0.874 / -0.409

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

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

Table 2

Selected geometric parameters (Å, deg.)
for compound 1

C6—N1	1.258(6)	N1—N2—C14	113.6(4)
C14—S1	1.760(6)	S1—C14—S2	123.4(3)
N1—N2	1.412(6)	C6—N1—N2	111.4(4)
C14—S2	1.761(6)	N2—C14—S2	122.4(4)
N2—C14	1.285(7)	C11—C6—N1	123.9(5)
		N2—C14—S1	113.6(4)
		C14—S2—C5	107.6(3)

Table 3

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

C26—C27	1.453(5)	C27—N3—N4	114.0(3)
N4—C28	1.281(4)	N4—C28—S4	121.5(3)
S3—C32	1.802(4)	N3—N4—C28	113.9(3)
C27—N3	1.267(4)	S3—C28—S4	122.8(2)
C28—S3	1.758(3)	C26—C27—N3	121.9(3)
S4—C29	1.798(4)	N4—C28—S3	115.5(3)
N3—N4	1.409(4)		
C28—S4	1.750(3)		

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. Elemental analyses 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 293(2) K and 296(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 the Lorentz and polarization effects. Semi-empirical 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]. The N2, C12, S1, S2, C12, C13, C14, C15, and C16 atoms in compound 2 are disordered over two positions. The site occupancy factor of N2 is 0.46 and 0.54, those of C12, C13, C14, C15, S1, and S2 are 0.5 and 0.5, and of C16 are 0.62 and 0.38 respectively. Hydrogen atoms were generated geometrically. Details of the crystal parameters are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3 respectively.

RESULTS AND DISCUSSION

As displayed in Fig. 1, titled compound 1 crystallized in the orthorhombic crystal system and a $Pca2_1$ space group.

For the ferrocenyl moiety, the distance from Fe(II) to the center of the substituted cyclopentadiene ring (C_{ps}) is 1.654(5) Å, while the distance of 1.376(2) Å is for the unsubstituted one (C_p). The C_{ps} —Fe— C_p bond angle is 173.65(8) Å, which means that central Fe(II) locates almost in the middle of the two cyclopentadiene rings. Besides, two cyclopentadiene rings are not parallel to each other with a slight dihedral angle to be only 1.37(3) Å.

The C6—N1, N1—N2, and C14—N2 bond distances are measured to be 1.258(6) Å, 1.412(6) Å and 1.285(7) Å, indicating that C6=N1 and C14=N2 are double bonds while N1—N2 is a single bond.

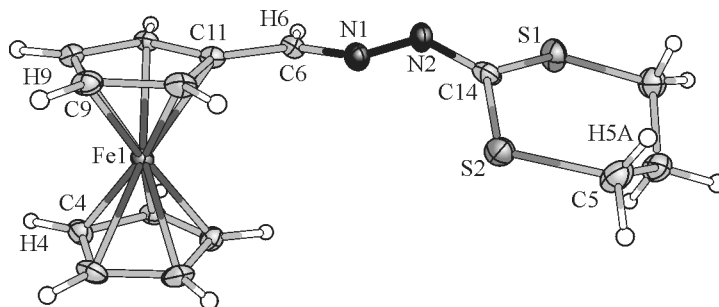


Fig. 1. Molecular structure of compound 1 with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

Hydrogen bonding geometry for compound **1** (Å, deg.)

Entry	D—H···A	D···H	H···A	D···A	D—H···A	Symmetry Codes
1	C4—H4···S1'	0.98	2.99	3.827(2)	142	
2	C5—H5A···N2'	0.97	2.56	3.501(9)	164	$x, 1+y, z$
3	C9—H9···S1'	0.98	2.87	3.762(6)	152	$3/2-x, y, -1/2+z$

Although no intramolecular hydrogen bonds are revealed for compound **1**, three intermolecular hydrogen bonds are found, as collected in Table 4. A one-dimensional zigzag chain can be constructed by C4—H4···S1', as shown in Fig. 2. The C4—H4, H4···S1', and C4···S1' bond lengths are 0.98 Å, 2.99 Å, and 3.827(2) Å respectively, while the bond angle is 142°. The other two intermolecular hydrogen bonds C5—H5A···N2' and C9—H9···S1' are used to form a two-dimensional network, as drawn in Fig. 2. The corresponding bond distances for C5—H5A, H5A···N2', C5···N2' and C9—H9, H9···S1', C9···S1' are found to be 0.97 Å, 2.56 Å, 3.501(9) Å and 0.98 Å, 2.87 Å, 3.762(6) Å. The bond angles are 164° and 152° respectively.

As for compound **2**, Fig. 3 gives the crystallized structure with a monoclinic crystal system and a $P2_1/c$ space group. Similar values were found for the ferrocenyl moiety; C_{ps} —Fe and C_p —Fe are 1.650 Å and 1.651 Å respectively. The C_{ps} —Fe— C_p bond angle is 178.72(1)°, and the dihedral angle

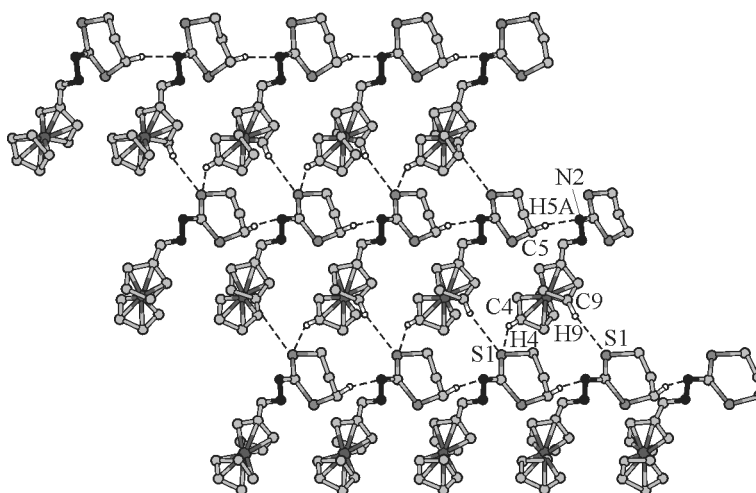


Fig. 2. Two-dimensional network of compound **1** organized by two intermolecular C5—H5A···N2' and C9—H9···S1' hydrogen bonds

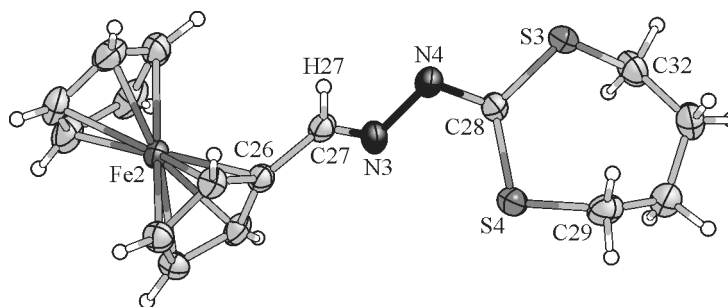


Fig. 3. Molecular structure of compound **2** with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

between two cyclopentadienes is $2.10(6)^\circ$. Due to the disorders of compound **2**, the one-dimensional zigzag chain and a two-dimensional network cannot be constructed.

Supplementary material. CIF file containing complete information on the studied structure was deposited with CCDC, deposition numbers 910724 and 910725, and is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

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PhCl salt is a superconducting salts can be obtained from a dithiane semiconductor with a thermal activation energy of 0.11 eV analog of BDH-TTP, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6- (rrt=2.0 10² S cm⁻¹) and exhibits Curie-Weiss behavior tetrathiapentalene (BDA-TTP, Fig. 1), in combination (C=4.42 emu K mol⁻¹, h=0.35 K). # 2002 Elsevier Science (USA) with relatively large anions such as SbF₆⁻; AsF₆⁻; and Key Words: non-TTF donor; crystal structure; conductivity; PF₆⁻ (6). Our attention was thus focused on the Fe- magnetic susceptibility; metallic behavior; antiferromagnetic containing BDH-TTP and BDA-TTP salts. Removal of a dithiane protection group often requires harsh conditions and is usually performed in the late synthetic stage. Summary of the use of 1,3-dithianes in synthesis. Protection of Carbonyl Compounds. A Lewis acid-surfactant-combined copper bis(dodecyl sulfate) [Cu(DS)₂] catalyst served as an efficient and reusable catalyst for the thioacetalization and transthioacetalization of carbonyl compounds and O,O-acetals in water at room temperature. Easily prepared 2-alkyl-1,3-dithiane derivatives were reacted with BrF₃ to form the corresponding 1,1-difluoromethyl alkanes in good yield. The reaction proceeds well with primary alkyl halides. The limiting step for secondary alkyl halides is the relatively low yield of the dithiane preparation. R. Sasson, A. Hagooly, S. Rozen, Org. Epoxides react with organomagnesium halides to afford a primary alcohol with the lengthening of the carbon chain by two carbon atoms. However, in this case of substituted epoxides, the attack of the organomagnesium halide takes place from the less substituted ring carbon atom of the epoxides (Scheme 7). 3.1.2.1 Reactions with Carbonyl Compounds. Organolithium reacts with aldehydes, ketones and esters to give alcohols as organomagnesium halides (Scheme 5). CO₂Et.