Weiping Liu*

Crystal structure of 2-(bis(4-fluorophenyl)methylene)hydrazine-1-carbothioamide, $C_{14}H_{11}F_2N_3S$

Table 1: Crystal collection and handling.

Crystal:	Block, colorless
Size:	0.25 × 0.23 × 0.20 mm
Wavelength:	Mo K α radiation ($\lambda = 0.71073$ Å)
μ :	0.247 mm $^{-1}$
Diffractometer, scan mode:	Bruker APEX-II CCD, ϕ and ω -scans
$\theta_{\max}$, completeness:	25.00°, 100%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7800, 2458, 0.0242
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2186
$N(\text{param})_{\text{refined}}$:	181
Programs:	Bruker [1], SHELX [2]

<https://doi.org/10.1515/ncrs-2018-0214>

Received June 23, 2018; accepted August 3, 2018; available online September 5, 2018

Abstract

$C_{14}H_{11}F_2N_3S$, monoclinic, $C2/c$ (no. 15), $a = 18.5399(19)$ Å, $b = 9.5907(10)$ Å, $c = 16.8149(17)$ Å, $\beta = 111.307(2)^\circ$, $V = 2785.5(5)$ Å 3 , $Z = 8$, $R_{\text{gt}}(F) = 0.0390$, $wR_{\text{ref}}(F^2) = 0.1317$, $T = 293(2)$ K.

CCDC no.: 1860150

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by the reaction of hydrazinecarbothioamide (1 mmol, 91.1 mg) with bis(4-fluorophenyl)methanone (1 mmol, 218.2 mg) in ethanol (15 mL) containing catalytic amounts of glacial acetic acid under reflux conditions (353 K) for 3 h. When cooled to room temperature, the solution was filtrated and then stand

at room temperature. After about 3 days, colourless block crystals were obtained.

Experimental details

All H atoms were geometrically placed in calculated positions ($C-H = 0.93$ Å, $N-H = 0.86$ Å) and refined as riding atoms, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atoms.

Discussion

As one important kind of Schiff-bases, thiosemicarbazones constitute an important class of N, S donor ligands and have gained more and more attention in recent years not only because of their chemistry, but also their biological activities [3–14]. Compared with the traditional thiosemicarbazones, the fluorine-containing thiosemicarbazones may exhibit other biological activities because of the inclusion of fluorine atoms in the molecules often has a great influence on their physical and chemical properties. But the fluorine-containing thiosemicarbazones are not well studied [11, 15]. In order to search for new thiosemicarbazones containing fluorine atoms, the title compound was synthesized.

There is one title molecule in the asymmetric unit. The $C13=N3$ bond distance in the molecule of $1.287(2)$ Å exhibits the expected value for a double-bond. The $C14=S1$ bond distance in the molecule is $1.6768(16)$ Å, which is between the typical $C-S$ single-bond (1.82 Å) and the typical $C=S$ double-bond (1.56 Å), thus reflecting a partial double bond character. The $C=N-N$ angle of $118.20(12)^\circ$ ($C13=N3-N2$) is smaller

*Corresponding author: Weiping Liu, Changsha Environmental Protection College, Changsha 410004, Hunan, People's Republic of China, e-mail: weipingliu18@126.com

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
S1	0.40582(2)	0.97556(5)	1.12682(3)	0.0512(2)
F1	0.74160(9)	0.39767(16)	0.89571(11)	0.0984(5)
F2	0.20944(7)	0.69860(18)	0.68459(9)	0.0920(5)
N1	0.54461(8)	0.86275(18)	1.16615(10)	0.0587(4)
H1A	0.5782	0.8150	1.1535	0.070
H1B	0.5561	0.8955	1.2169	0.070
N2	0.46162(8)	0.83120(16)	1.02977(8)	0.0457(4)
H2A	0.4175	0.8437	0.9894	0.055
N3	0.51857(7)	0.75549(14)	1.01526(8)	0.0423(3)
C1	0.56551(9)	0.61877(15)	0.92831(10)	0.0377(4)
C2	0.64247(9)	0.65024(18)	0.97601(11)	0.0440(4)
H2	0.6539	0.7230	1.0152	0.053
C3	0.70198(10)	0.5754(2)	0.96604(13)	0.0539(5)
H3	0.7533	0.5958	0.9985	0.065
C4	0.68358(12)	0.4702(2)	0.90702(14)	0.0604(5)
C5	0.60895(13)	0.4351(2)	0.85866(14)	0.0625(5)
H5	0.5985	0.3622	0.8197	0.075
C6	0.54932(11)	0.51068(18)	0.86910(12)	0.0497(4)
H6	0.4982	0.4891	0.8364	0.060
C7	0.42325(9)	0.69630(15)	0.87373(10)	0.0364(4)
C8	0.36178(11)	0.6305(2)	0.88556(12)	0.0584(5)
H8	0.3692	0.5859	0.9371	0.070
C9	0.28938(11)	0.6299(2)	0.82191(14)	0.0657(6)
H9	0.2479	0.5850	0.8296	0.079
C10	0.28025(10)	0.6968(2)	0.74770(12)	0.0535(5)
C11	0.33862(10)	0.7645(2)	0.73339(11)	0.0526(4)
H11	0.3302	0.8100	0.6819	0.063
C12	0.41110(9)	0.76395(18)	0.79759(10)	0.0444(4)
H12	0.4520	0.8097	0.7893	0.053
C13	0.50189(9)	0.69505(15)	0.94241(10)	0.0374(4)
C14	0.47545(9)	0.88571(16)	1.10779(10)	0.0413(4)

than the expected 120°. The dihedral angle formed by the two phenyl rings is 80.6°. In the crystal structure, a dimer structure is formed by the N—H···S hydrogen bonds. The adjacent dimers are further linked into infinite chains by weak C—H···S hydrogen bonds. In addition, very weak N—H···F hydrogen bonds link these chains into layers.

Acknowledgements: This work was financial supported by Changsha Environmental Protection College.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2008).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.

3. Lobana, T. S.; Sharma, R.; Bawa, G.; Khanna, S.: Bonding and structure trends of thiosemicarbazone derivatives of metals-an overview. *Coord. Chem. Rev.* **253** (2009) 977–1055.
4. Haribabu, J.; Subhashree, G. R.; Saranya, S.; Gomathi, K.; Karvembu, R.; Gayathri, D.: Isatin based thiosemicarbazone derivatives as potential bioactive agents: Anti-oxidant and molecular docking studies. *J. Mol. Struct.* **1110** (2016) 185–195.
5. Idemudia, O. G.; Sadimenko, A. P.; Hosten, E. C.: Crystal structure of 4-propyl-3-methyl-1-phenyl-2-pyrazolin-5-one thiosemicarbazone, C₁₅H₁₉N₅OS. *Z. Kristallogr. NCS* **230** (2015) 81.
6. Liu, C.: Crystal structure of (*E*)-2-(anthracen-9-ylmethylene)hydrazinecarbothioamide, C₁₆H₁₃N₃S. *Z. Kristallogr. NCS* **233** (2018) 315–316.
7. Netalkar, P. P.; Netalkar, S. P.; Revankar, V. K.: Transition metal complexes of thiosemicarbazone: synthesis, structures and invitro antimicrobial studies. *Polyhedron* **100** (2015) 215–222.
8. Kate, A. N.; Kumbhar, A. A.; Khan, A. A.; Joshi, P. V.; Puranik, V. G.: Monitoring cellular uptake and cytotoxicity of copper(II) complex using a fluorescent anthracene thiosemicarbazone ligand. *Bioconjug. Chem.* **25** (2014) 102–114.
9. Pelosi, G.: Thiosemicarbazone metal complexes: from structure to activity. *Open Crystallogr. J.* **3** (2010) 16–28.
10. Lovejoy, D. B.; Sharp, D. M.; Seebacher, N.; Obeidy, P.; Prichard, T.; Stefani, C.; Basha, M. T.; Sharpe, P. C.; Jansson, P. J.; Kalinowski, D. S.; Bernhardt, P. V.; Richardson, D. R.: Novel second-generation di-2-pyridylketone thiosemicarbazones show synergism with standard chemotherapeutics and demonstrate potent activity against lung cancer xenografts after oral and intravenous administration *in vivo*. *J. Med. Chem.* **55** (2012) 7230–7244.
11. Bautista, J. L.; Flores-Alamo, M.; Tiburcio, J.; Vieto, R.; Torrens, H.: Synthesis and structural characterization of fluorinated thiosemicarbazones. *Molecules* **18** (2013) 13111–13123.
12. Pape, V. F. S.; Tóth, S.; Füredi, A.; Szebényi, K.; Lovrics, A.; Szabó, P.; Wiese, M.; Szakács, G.: Design, synthesis and biological evaluation of thiosemicarbazones, hydrazinobenzothiazoles and arylhydrazones as anticancer agents with a potential to overcome multidrug resistance. *Eur. J. Med. Chem.* **117** (2016) 335–354.
13. King, A. P.; Gellineau, H. A.; Ahn, J. E.; MacMillan, S. N.; Wilson, J. J.: Bis(thiosemicarbazone) complexes of Cobalt(III). Synthesis, characterization, and anticancer potential. *Inorg. Chem.* **56** (2017) 6609–6623.
14. Gatti, A.; Habtemariam, A.; Romero-Canelón, I.; Song, J. I.; Heer, B.; Clarkson, G. J.; Rogolino, M.; Sadler, P. J.; Carcelli, M.: Half-Sandwich Arene Ruthenium(II) and Osmium(II) Thiosemicarbazone complexes: solution behavior and antiproliferative activity. *Organometallics* **37** (2018) 891–899.
15. Kumar, G. D. K.; Chavarria, G. E.; Charlton-Sevcik, A. K.; Arispe, W. M.; MacDonough, M. T.; Strecker, T. E.; Chen, S. E.; Siim, B. G.; Chaplin, D. J.; Trawick, M. L.; Pinney, K. G.: Design, synthesis, and biological evaluation of potent thiosemicarbazone based cathepsin L inhibitors. *Bioorg. Med. Chem. Lett.* **20** (2010) 1415–1419.