Crystal structure of (2-picoloylcarbonyl)thiosemicarbazone, $C_7H_{10}N_4O_2S$

W.-S. Wu*,[I] and Y.-L. Feng[II]

[I] Huaqiao University, College of Materials, Quanzhou, Fujian, 362011 P. R. China
[II] Zhejiang Normal University, Institute of Physical Chemistry, Jinhua, Zhejiang, 321004 P. R. China

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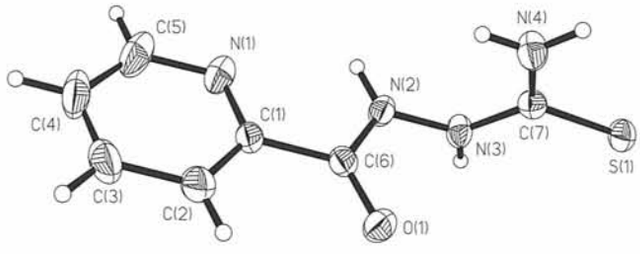

Abstract

$C_7H_{10}N_4O_2S$, orthorhombic, *Pbca* (No. 61), $a = 12.1705(9)$ Å, $b = 7.421(2)$ Å, $c = 22.7584(5)$ Å, $V = 2055.3$ Å^3, $Z = 8$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.075$, $T = 293$ K.

Source of material

The title compound was synthesized by refluxing an equimolar mixture of 2-picoloylhydrazine and thiosemicarbazide in ethanol for 1 h. Single crystals suitable for the X-ray structure analysis were obtained from ethanol.

Experimental details

The U_{ij} values for the neighboring positions C3, C4 and C5 are rather large. We cannot explain this structural feature.

Discussion

Compared to simple hydrazone Schiff base, acyl, aroyl and heteroaroyl Schiff base have an additional O-donor atom from the carbonyl group, whose presence introduces a wider range of properties [1]. These compounds may therefore function as polydentate ligands and some reports of their complexes have appeared [2].

The molecule of title compound is non-planar (twisted) and consists of a planar 2-picolonybonyl group (r.m.s. deviation 0.030 Å) and a thiosemicarbazone group (r.m.s. deviation 0.014 Å), the dihedral angle between them being 83.09(5)°. The C6—N2 bond length of 1.340(2) Å is essentially the same as C7—N3 of 1.338(2) Å, indicating that C6—N2 is single bond. The N2—N3 bond length of 1.387(2) Å in the title compound is in good agreement with N—N one in the compounds of *N*,*N*′-bis(picolonoyl)hydrazine [3] and propionylpicoloylhydrazide [4]. To form the two-dimensional structure, the molecules connected to each other through intramolecular and intermolecular hydrogen bonds with d(N3···O2) = 2.784 Å and ∠N3–H3···O2 = 138.3°, d(O2···S1^a) = 3.333 Å and ∠O2–H21···S1^a = 163.6°, d(O2···O1^b) = 2.964 Å and ∠O2–H22···O1^b = 158.3°, d(N2···S1^c) = 3.380 Å and ∠N2–H2···S1^c = 143.6°, d(N4···O1^d) = 3.007 Å and ∠N4–H41···O1^d = 158.0°, d(N4···S1^d) = 3.383 Å and ∠N4–H42···S1^d = 155.9° (*a*: –*x*+1, –*y*+1, –*z*; *b*: –*x*+1/2, *y*+1/2, *z*; *c*: –*x*+1, –*y*, –*z*; *d*: –*x*+1/2, *y*–1/2, *z*).

Table 1. Data collection and handling.

Crystal:	colurless prism, size 0.06 × 0.09 × 0.59 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	2.97 cm^{-1}
Diffractometer, scan mode:	Riguku R-AXIS RAPID, ω/φ
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2352, 2352
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1289
$N(param)_{refined}$:	127
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(21)	8*c*	0.5069	0.5824	0.0654	0.099
H(22)	8*c*	0.4012	0.5628	0.0933	0.099
H(2)	8*c*	0.4581	0.0190	0.1078	0.049
H(3)	8*c*	0.4407	0.2546	0.0319	0.049
H(41)	8*c*	0.3178	–0.1365	0.0390	0.059
H(42)	8*c*	0.2870	–0.1516	–0.0242	0.059
H(2)	8*c*	0.1891	0.1447	0.2219	0.067
H(3)	8*c*	0.2183	0.0561	0.3192	0.092
H(4)	8*c*	0.3854	–0.0678	0.3442	0.097
H(5)	8*c*	0.5180	–0.1038	0.2731	0.085

* Correspondence author (e-mail: wuwenshi@sohu.com)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*c*	0.36378(4)	0.15871(6)	–0.07436(2)	0.0522(3)	0.0478(2)	0.0306(2)	0.0001(3)	0.0025(2)	0.0036(2)
O(1)	8*c*	0.2402(1)	0.2104(2)	0.11533(5)	0.0507(8)	0.0587(8)	0.0438(6)	0.0164(7)	–0.0010(7)	0.0065(6)
O(2)	8*c*	0.4523(1)	0.5087(2)	0.07018(7)	0.071(1)	0.0598(9)	0.116(1)	–0.0189(9)	0.013(1)	–0.0182(9)
N(1)	8*c*	0.4365(2)	–0.0025(2)	0.20670(6)	0.055(1)	0.058(1)	0.0454(9)	–0.003(1)	–0.0125(9)	0.0103(8)
N(2)	8*c*	0.4059(1)	0.0874(2)	0.09554(6)	0.044(1)	0.0462(8)	0.0312(7)	0.0066(8)	–0.0012(7)	0.0068(7)
N(3)	8*c*	0.4084(1)	0.1536(2)	0.03857(5)	0.049(1)	0.0436(8)	0.0291(7)	–0.0082(8)	0.0007(6)	0.0051(7)
N(4)	8*c*	0.3171(1)	–0.0924(2)	0.00405(6)	0.064(1)	0.0464(9)	0.0374(7)	–0.0180(9)	–0.0031(8)	0.0040(7)
C(1)	8*c*	0.3387(2)	0.0695(2)	0.19371(7)	0.052(1)	0.0354(9)	0.0313(8)	0.0000(9)	–0.0032(8)	–0.0018(7)
C(2)	8*c*	0.2556(2)	0.0941(3)	0.23335(7)	0.077(1)	0.047(1)	0.0431(9)	0.006(1)	0.010(1)	0.0030(9)
C(3)	8*c*	0.2730(3)	0.0414(3)	0.29113(8)	0.134(2)	0.058(1)	0.038(1)	–0.001(2)	0.023(2)	0.001(1)
C(4)	8*c*	0.3715(3)	–0.0319(3)	0.30572(9)	0.148(3)	0.061(1)	0.033(1)	–0.019(2)	–0.021(2)	0.006(1)
C(5)	8*c*	0.4511(2)	–0.0525(3)	0.26259(9)	0.084(2)	0.071(1)	0.059(1)	–0.013(2)	–0.036(1)	0.019(1)
C(6)	8*c*	0.3225(2)	0.1290(2)	0.13154(7)	0.045(1)	0.0352(9)	0.0338(8)	–0.0013(9)	–0.0001(8)	–0.0024(8)
C(7)	8*c*	0.3622(1)	0.0650(2)	–0.00626(7)	0.031(1)	0.0397(9)	0.0354(8)	0.0009(9)	0.0036(8)	–0.0010(8)

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