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CRYSTAL STRUCTURE OF THE ACETIC ACID SOLVATE OF N-(PROP-2-EN-1-YL)-2-(PYRID-2-YLMETHYLIDENE)HYDRAZINECARBOSELENOAMIDE

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The crystal structure of the acetic acid solvate of N-(prop-2-en-1-yl)-2-(pyrid-2-ylmethylidene)hydrazinecarboselenoamide (**I**) is determined. The asymmetric unit of the unit cell in its crystal structure contains a molecule of **I** and an acetic acid molecule. The molecule of **I** is non-planar; the angle between the mean square planes of hydrazinecarboselenoamide *A*(Se1N1N2N3C1C2) and prop-2-en-1-yl (C5C6C7) moieties is 82.3°. In the crystal, the acetic acid molecules link the molecules of **I** in endless chains along the [010] direction.

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Selenosemicarbazones and their derivatives are the compounds exhibiting a high biological activity, which in many cases, surpasses the activity of the corresponding sulfur-containing analogs [1]. It is shown in some works [2, 3] that the biological activity of the compounds is well consistent with their structure. Therefore, the synthesis and study of the structural features of new selenosemicarbazones are of scientific and practical interest.

The aim of the present work was to synthesize and determine the structural features of the acetic acid solvate of N-(prop-2-en-1-yl)-2-(pyrid-2-ylmethylidene)hydrazinecarboselenoamide (**I**).

EXPERIMENTAL

Compound **I** is synthesized by the following procedure. Sodium borohydride (0.151 g, 4.0 mmol) and 0.119 g of selenium powder (1.5 mmol) were mixed in a water-ethanol solution in the argon atmosphere. The reaction resulted in the formation of a sodium hydroselenide solution [4]. The optimum value for the nucleophilic substitution reaction pH = 8-9 was maintained by adding an ammonia buffer solution to the reaction mixture. When the total amount of selenium dissolved, an ethanol solution of 0.234 g (1 mmol) of 4-allyl-S-methylisothiosemicarbazone 2-formylpyridine was added to the solution. The solution obtained was heated and magnetically stirred for 30 h in the argon atmosphere. Then the solution was cooled and neutralized with concentrated acetic acid. The target reaction product was extracted with three portions of chloroform (10 ml each). Evaporation of the solution resulted in the formation of an orange fine crystalline precipitate, which was filtered off and dried in the air. Its composition was determined based on the elemental analysis data.

Found, %: C 44.32; H 4.81; N 17.34. For $C_{12}H_{16}N_4O_2Se$, calculated, %: C 44.04; H 4.93; N 17.12.

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^{1}H NMR (DMSO-d^6): 12.07 (br s, 1H, NH); 11.86 (br s, 1H, COOH); 9.28 (br s, 1H, NH); 8.59 (d, CH arom.); 8.31 (d, CH arom.); 8.22 (s, 1H, CH=N); 7.90 (t, 1H, CH arom.); 7.44 (t, 1H, CH arom.); 5.93 (m, 1H, CH allylic); 5.16 (m, 2H, CH_2=C); 4.33 (m, 2H, CH_2-N); 1.92 (s, 3H, CH_3).

^{13}C NMR (DMSO-d^6): 176.35 (C=Se); 172.30 (COOH); 153.16, 149.44, 137.70, 124.94, 121.35 (C, arom); 143.41 (CH=N); 135.04 (CH allylic); 116.45 (CH_2=); 48.88 (CH_2-N); 20.50 (CH_3).

The compound is well-soluble in DMFA and DMSO, EtOH, MeOH, $CHCl_3$. Single crystals suitable for an X-ray diffraction analysis were obtained by recrystallization from the EtOH/$CHCl_3$ mixture.

A single crystal X-ray diffraction analysis of compound **I** was performed on an Xcalibur diffractometer (Oxford Diffraction) [5]. The structure was solved by the direct method and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the SHELX-97 programs [6]. The hydrogen atoms were placed in geometrically idealized positions, and their thermal parameters U_H were considered to be 1.2 times as much as those of the carbon and oxygen atoms bonded to them. The selected interatomic distances and bond angles are listed in Table 1; the coordinates of base atoms of the structure under study have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1533963). The hydrogen bonds parameters are listed in Table 2. The geometric calculations and figures were carried out using the PLATON program [7]. The analysis of the hydrogen bonds was carried out according to the following criteria [7-9]:

$$d(\text{D}\ldots\text{A}) < R(\text{D}) + R(\text{A}) + 0.5\ \text{Å},\ d(\text{H}\ldots\text{A}) < R(\text{H}) + R(\text{A}) - 0.12\ \text{Å},\ \text{D–H}\ldots\text{A} > 100.0°.$$

$C_{12}H_{16}N_4O_2Se$: the sample size was 0.35×0.15×0.12 mm, MoK_α radiation (λ = 0.71073 Å), M = 327.25, orthorhombic crystal system, space group *Pbcn*, a = 7.9579(6) Å, b = 17.0661(10) Å, c = 22.2595(12) Å, V = 3023.1(3) Å^3; Z = 8, ρ_{calc} = 1.438 g/cm^{-3}, μ = 2.488 mm^{-1}, 7687 reflections measured (θ_{max} = 25.05°), including 2687 independent ones, 1207 reflections with $I > 2\sigma(I)$, 176 parameters refined, for $I > 2\sigma(I)$ R_1 = 0.067 and wR_2 = 0.139, $\Delta\rho$(max/min) = 0.331 / -0.346 e/Å^3.

RESULTS AND DISCUSSION

The asymmetric unit of the unit cell in the crystal structure contains an N-(prop-2-en-1-yl)-2-(pyrid-2-ylmethylidene)hydrazinecarboselenoamide molecule (**I**) and a solvate molecule of acetic acid (Fig. 1). In **I**, the substituents located relative to N2–C1 carbamide bonds and N1–C2 azomethine bonds are at the *E*-position. The *A*(Se1N1N2N3C1C2)

TABLE 1. Selected Interatomic Distances and Bond Angles in the Molecule of **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Se(1)–C(1)	1.823(6)	N(3)–C(1)	1.318(7)	C(4)–C(8)	1.391(8)
N(1)–C(2)	1.271(6)	N(3)–C(5)	1.448(7)	C(5)–C(6)	1.422(9)
N(1)–N(2)	1.368(6)	C(3)–C(10)	1.376(7)	C(7)–C(6)	1.331(11)
N(4)–C(4)	1.321(7)	C(3)–C(2)	1.459(7)	O(1C)–C(1C)	1.194(7)
N(4)–C(3)	1.346(6)	C(9)–C(10)	1.366(8)	O(2C)–C(1C)	1.308(7)
N(2)–C(1)	1.343(7)	C(9)–C(8)	1.375(9)	C(2C)–C(1C)	1.494(8)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
C(2)–N(1)–N(2)	117.6(5)	N(1)–C(2)–C(3)	121.3(5)	C(9)–C(8)–C(4)	118.1(6)
C(4)–N(4)–C(3)	118.0(5)	N(3)–C(1)–N(2)	116.5(5)	C(6)–C(5)–N(3)	110.7(6)
C(1)–N(2)–N(1)	119.6(5)	N(3)–C(1)–Se(1)	124.9(5)	C(7)–C(6)–C(5)	120.9(9)
C(1)–N(3)–C(5)	125.0(5)	N(2)–C(1)–Se(1)	118.6(5)	O(1C)–C(1C)–O(2C	123.7(6)
N(4)–C(3)–C(10)	121.9(6	C(10)–C(9)–C(8)	119.0(6)	O(1C)–C(1C)–C(2C)	123.9(6)
N(4)–C(3)–C(2)	117.8(5)	C(9)–C(10)–C(3)	119.7(6)	O(2C)–C(1C)–C(2C)	112.4(6)
C(10)–C(3)–C(2)	120.3(6)	N(4)–C(4)–C(8)	123.2(6)		

TABLE 2. Geometric Parameters of the Hydrogen Bonds

No.	Bond D–H…A	Distance, Å			DHA angle, deg	Coordinates of the A atom
		D…A	H…A	D–H		
1	N(2)–H(2)…O(1C)	2.917	2.15	0.77	174	1/2–*x*, 1/2+*y*, *z*
2	O(2C)–H(2C)…N(4)	2.688	1.87	0.82	176	*x*, *y*, *z*
3	N(3)–H(3)…O(2C)	3.048	2.21	0.86	166	*x*, *y*, *z*
4	N(3)–H(3)…N(1)	2.608	2.21	0.86	108	*x*, *y*, *z*
5	C(4)–H(4)…O(1C)	3.240	2.55	0.93	131	*x*, *y*, *z*
6	C(5)–H(5B)…Se(1)	3.206	2.73	0.97	111	*x*, *y*, *z*

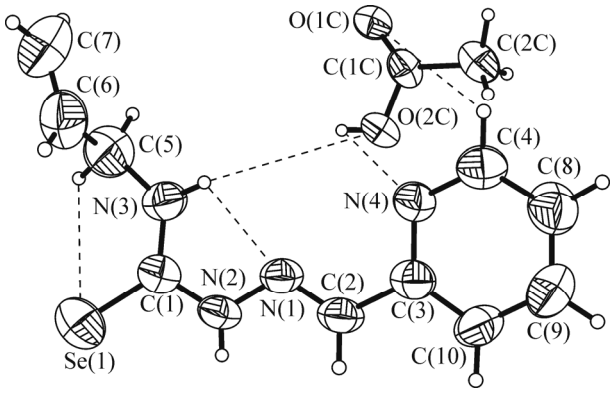


Fig. 1. Atomic numbering in compound **I**.

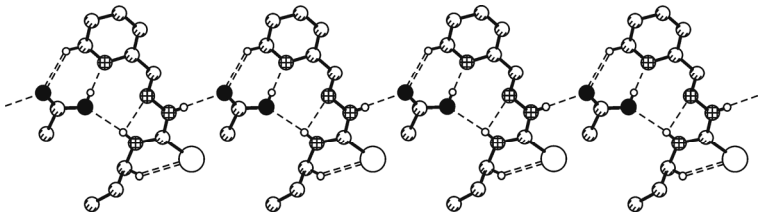


Fig. 2. Formation of chains along the [010] direction.

moiety in **I** is nearly planar; deviations of the atoms from the planes they determine do not exceed 0.025 Å. The pyridine ring plane is oriented relative to the *A* moiety at an angle of 3.0°. The N4 atom of this ring is in the *cis* position relative to the N1 atom; the corresponding torsion angle N1–C2–C3–N4 is 2.3°. However, in general, the N-(prop-2-en-1-yl)-2-(pyrid-2-ylmethylidene)hydrazinecarboselenoamide molecule is non-planar; the angle between the mean square planes of the *A* and (C5C6C7) moieties is 82.3°. In this case, the values of the bond lengths in *A* (Table 1) indicate their delocalization.

In the crystal, the solvate molecules of acetic acid link the N-(prop-2-en-1-yl)-2-(pyrid-2-ylmethylidene)hydrazinecarboselenoamide molecules into endless chains along the [010] direction through the N(2)–H(2) …O(1C) and O(2C)–H(2C) …N(4) hydrogen bonds (Fig. 2). Apart from van der Waals interactions, there is also an X–H…Cg(π ring) interaction (H···Cg < 3.0 Å, γ < 30.0°, where γ is the angle between the H···Cg vector and the normal to the aromatic ring [7, 10]) between the chains linked by the twofold rotation axis. Thus, for the interaction C(5)–H(5A)···Cg(pyridine) (1–*x*, *y*, 1/2–*z*), the distance between the H(5A) atom and the centroid of the pyridine ring is 2.86 Å and γ = 1.4°.

REFERENCES

1. C. Pizzo, P. Faral-Tello, G. Salinas, M. Fló, C. Robello, P. Wipf, and S. G. Mahler. *Med. Chem. Comm*., **2012**, *3*, 362.
2. S. R. Turk, C. Shipman Jr., and J. C. Drach. *J. Gen. Virol*., **1986**, *67*, 1625.
3. D. S. Kalinowski, P. Quach, and D. R. Richardson. *Future Med. Chem*., **2009**, *1*, 1143.
4. D. L. Klayman and T. S. Griffin. *J. Am. Chem. Soc*., **1973**, *95*, 197.
5. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52 (release 06-11-2009 CrysAlis171.NET).
6. G. M. Sheldrich. *Acta Crystallogr*., **2008**, *A64*, 112.
7. A. L. Spek. *J. Appl. Crystallogr*., **2003**, *36*, 7.
8. Th. Steiner. *Cryst. Rev*., **1996**, *6*, 1.
9. G. A. Jeffrey, H. Maluszynska, and J. Mitra. *Int. J. Biol. Macromol*., **1985**, *7*, 336.
10. J. F. Malone, C. M. Murray, M. H. Charlton, R. Docherty, and A. J. Lavery. *J. Chem. Soc*., *Faraday Trans*., **1997**, 3429.