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A study on types of hydrogen bonding in crystal structure of 1-acetyl-3-thiosemicarbazide

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The unit cell structure of 1-acetyl-3-thiosemicarbazide (ATSC) and the types of hydrogen bonds present in crystalline form are envisaged from single crystal X-ray diffraction studies. The presence of four types of hydrogen bonds in crystal packing is evident (N─H· · ·O, N─H· · ·N, N─H· · ·S and O─H· · ·O) from the results obtained in present study. The topological analysis of hydrogen bonds indicated both inter- and intramolecular hydrogen bonding. Presence of water molecule is evident in its structure indicating that the title compound is in hydrated form. The single crystal X-ray diffraction data corresponding to hydrogen bonding reveals the hydrogen-bond strength sequence as: N─H· · ·N > O─H· · ·O > N─H· · ·O > N─H· · ·S.

Keywords: thiosemicarbazide, hydrogen, X-ray diffraction, crystal, hydrated form

The 1-acetyl-3 thiosemicarbazide (ATSC) was characterized by ^1H and ^{13}C NMR studies earlier from our laboratory. The results revealed the existence of compound in keto-enol forms[1] in solution. To understand the structure of ATSC, an attempt is made to develop crystals to study a single crystal X-ray diffraction pattern. Both the XRD and the Liquid Chromatography-Mass Spectrometry Hyphenated (LC-MS) techniques employed in the study revealed the molecular mass in support of the compound in mono hydrated form.

Materials and Methods

Crystal growth

1-Acetyl-3-thiosemicarbazide was synthesized following the known procedures[2,3]. The aqueous solution of ATSC was prepared and allowed for the slow evaporation by diffusion method in diethylether for the crystal growth.

LC-MS studies

The LC-MS data was collected on Shimadzu LCMS-2010A. The chromatogram was obtained by injecting 5 μL of the sample dissolved in methanol into C_{18} column, mobile phase: methanol:water mixture 90:10, with a flow rate 0.2 mL/min and UV (254 nm) detector. The mass spectrum is obtained by using atmospheric pressure chemical ionization in positive mode.

X-Ray Crystallography

High-resolution single crystal X-ray diffraction data was collected at 298 K on Bruker Smart APEX CCD diffratometer, area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube [λ(Mo-Kα) = 0.71073 Å]. A single crystal was mounted in a Lindemann capillary and 2400 frames were recoded with scanning angle ω of 0.3°, each for 5 sec exposure with 0.5 mm collimated X-ray. The crystal to detector distance was kept 60 mm for high resolution[4,5]. Collected data is reduced by SAINTPLUS[6], an empirical absorption correction was applied to the collected reflections with SADABS[7], the structures were solved with direct methods using SHELXS-97 (ref. 8) and the refinement done against F^2 using SHELXL-97 (ref. 9). The crystal-packing diagram was generated by mercury 1.4.1 of CCDC. All non-hydrogen atoms were refined anisotropically and hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms for water molecule were located in the difference Fourier maps and their positions were refined isotropically.

Results and Discussion

LC chromatogram of 1-acetyl-3-thiosemicarbazide showed a single peak at 0.631 min. Mass-*m/z*: 174(M+23, Na adduct), 156, 134, 132, 116,100, 84, 57.

1-Acetyl-3-thiosemicarbazide is a molecule having three nitrogen atoms, three carbon atoms, one oxygen atom, one sulphur atom and seven hydrogen atoms with a probability for hydrogen bonding interactions. Analysis of crystal structure obtained indicated the presence of one water molecule. The ORTEP[10] view of ATSC with labeling of non-hydrogen atoms is shown in **Figure 1**. The unit cell parameters, experimental details and refinement parameters are listed in **Table I**. The crystal system is monoclinic and $P2_1/c$ space group with four molecules of ATSC and four molecules of water. Analysis of bond lengths and bond angles (**Table II**) reveal that NH_2 of N(1) is coplanar with S(1)─C(1)─N(2)─N(3) plane. The crystal structure reveals the presence of four molecules per unit cell with epitome of two ways of orientation.

Nevertheless, ATSC molecule has less number of atoms; it has good number of hydrogen-bond donors and acceptors. There are six hydrogen bond donors (two hydrogen atoms from each of the group *viz*; thioamide, hydrazine and water) and four hydrogen bond acceptors ('S' of thiocarbonyl, 'O' of carbonyl, 'N' of hydrazine and 'O' of water), thus making the molecular surface embellished with hydrogen bonds. All the hydrogen atoms were located from difference Fourier maps. Interaction metrics at 298 K are given in **Table III**.

Topological analysis of hydrogen bonding showed the presence of four types of hydrogen bonds: N─H· · ·O, N─H· · ·N, N─H· · ·S and O─H· · ·O. In this hydrogen bonding, the N─H· · ·N interactions are intramolecular while other three are of intermolecular type[11]. Careful analysis of the structure reveals that one molecule of ATSC is associated with another molecule of it through hydrogen bonding by weak N(2)–H(2)· · · S(1) interactions with H· · ·S bond distance of 2.54Å and vice versa as shown in **Figure 2a**. These N—H· · ·S synthons further interacts via N(3)–H(3) · · ·S(1) hydrogen bond with H· · ·S distance of 2.56Å and vice versa (**Figure 2b**) to form zigzag network along crystallographic *bc* plane.

Similarly 1 N(1) —H(1A) · · ·O(2) and 1 N(1) —H(1B) · · ·O(2) interactions signify the H· · ·O bond lengths of 2.11 and 2.13Å respectively. A comparison of the bond lengths of H· · ·O and H· · ·S interaction reveals the fact that the former bond lengths are shorter than latter[12]. The hydrogen-bond strengths were found to be in the order: N─H· · ·N > O─H· · ·O > N─H· · ·O > N─H· · ·S. These results are in accordance with the earlier reported bond lengths of H· · ·O and H· · ·S for 1-formyl 3-thiosemicarbazide[13] implicating that sulphur being less electronegative than oxygen, would show weaker H· · ·S interactions than H· · ·O.

Water molecule is involved in hydrogen-bond interactions with parent moiety and two other ATSC molecules with H· · ·O bond distances of (O2—H8· · ·O1) 2.13Å and (O2—H9· · ·O1) 2.11Å respectively.

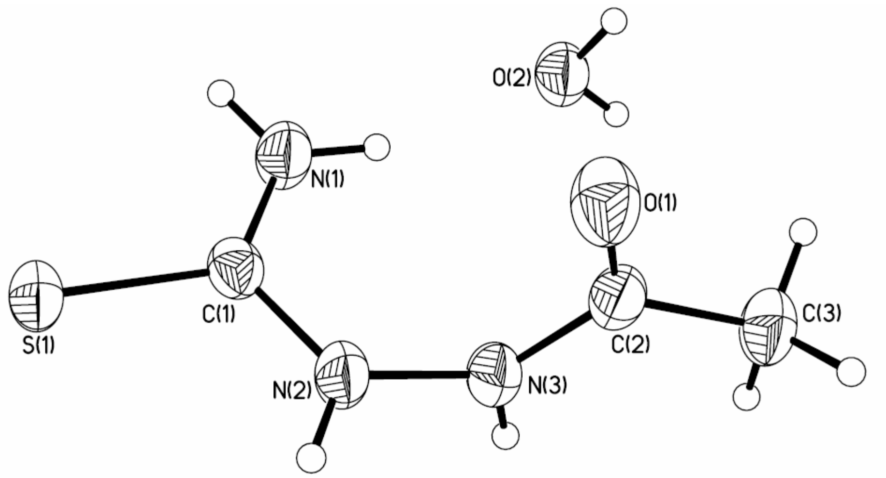


Figure 1 — Thermal ellipsoidal plot with 50% probability for non-H atoms

The oxygen atom of same water molecule acts as acceptor of hydrogen atoms of thioamide nitrogen atoms of two different ATSC molecules with H· · ·O bond distances of (N1-H1A· · ·O2) 2.11Å and (N1 —H1B· · ·O2) 2.13Å respectively. The geometric analysis revealed that the intramolecular N(1)—H(1A)· · ·N(3) interaction directs the molecular confirmation to bring N(1) nitrogen, H(1A) and H(1B) hydrogen atoms to be co-planar with S(1)─C(1)─N(2)─N(3) plane. Both the weak and strong hydrogen bonding interactions between ATSC and water molecule (**Figure 3**) leads to form a three dimensional network through ***b*** axis.

Table I — Single crystal X-ray diffraction data and structure refinement for 1-acetyl-3- thiosemicarbazide at 298 K

Crystal data

Empirical formula	$C_3H_9N_3O_2S$
Formula weight	151.19
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.1437(8)Å α = 90°
	b = 5.2066(5)Å β = 99.860(2)°
	c = 16.5182(16)Å γ = 90°
Volume	690.04(12) A^3
Z, Calculated density	4, 1.455 Mg/m^3
Absorption coefficient	0.403 mm^{-1}
F(000)	320
Crystal size	0.41 x 0.28 × 0.08 mm
Theta range for data collection	2.50 to 26.00 deg.
Limiting indices	–10 ⇒h⇒ 10, –6 ⇒k⇒ 6, –19⇒l⇒ 20
Reflections collected / unique	5833 / 1348 [R(int) = 0.0260]
Completeness to theta = 26.00	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9684 and 0.8521
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1348 / 0 / 99
Goodness-of-fit on F^2	1.067
Final R indices [I>2σ(I)]	R1 = 0.0307, wR2 = 0.0775
R indices (all data)	R1 = 0.0328, wR2 = 0.0797
Largest diff. peak and hole	0.175 and -0.294.A^{-3}

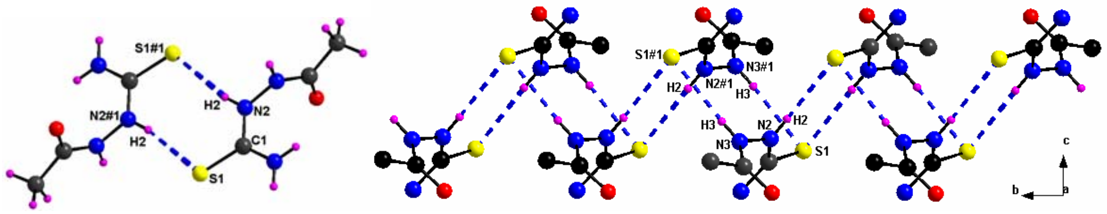
Table II — Bond lengths [Å] and angles [deg] for ATSC H_2O

Bond lengths	
C(1)-N(1)	1.3068(19)
C(1)-N(2)	1.344(2)
C(1)-S(1)	1.7054(14)
C(2)-N(3)	1.349(2)
C(2)-C(3)	1.495(2)
N(2)-N(3)	1.3869(18)
Bond angles	
N(1)-C(1)-N(2)	119.42(13)
N(1)-C(1)-S(1)	122.51(11)
N(2)-C(1)-S(1)	118.07(11)
O(1)-C(2)-N(3)	122.35(13)
O(1)-C(2)-C(3)	123.09(14)
C(1)-N(1)-H(1A)	120.0
C(1)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(1)-N(2)-N(3)	122.53(13)

Table III — Geometrical analysis of hydrogen bonding interactions

Res Donor—H.. Acceptor	**(ARU)**	**D—H (Å)**	**H...A(Å)**	**D...A (Å)**	**D—H...A (º)**
Intramolecular interactions					
1 N(1) —H(1A)··N(3)	( )	0.86	2.42	2.7398(19)	103
Intermolecular interactions					
1 N(1) —H(1A)··O(2)	(3)	0.86	2.11	2.9384(19)	161
1 N(1) —H(1B)··O(2)	(4)	0.86	2.13	2.9682(18)	165
1 N(2) —H (2) ··S(1)	(1)	0.83(2)	2.54(2)	3.3453(16)	167.4(16)
1 N(3) —H (3) ··S(1)	(2)	0.85(2)	2.56(2)	3.3972(15)	173.5(19)
2 O(2) —H (8) ··O(1)	(5)	0.81(2)	2.13(2)	2.9142(17)	165(2)
2 O(2) —H (9) · ·O(1)	( )	0.77(2)	2.11(3)	2.8685(16)	172(2)

Translation of ARU-code to equivalent position code
(1) = 1-x,1-y,1-z; (2) = 1-x,-y,1-z; (3) = x,-1+y,z; (4) = 1-x,-1/2+y,1/2-z; (5) = -x,1/2+y,1/2-z



2a.

2b

Figure 2: N2─H2· · ·S1 interactions with symmetry codes 1#1-x, -y, 2-z, and N3─H3· · ·S1 interactions with symmetry codes 1#1-x, -y, 2-z.

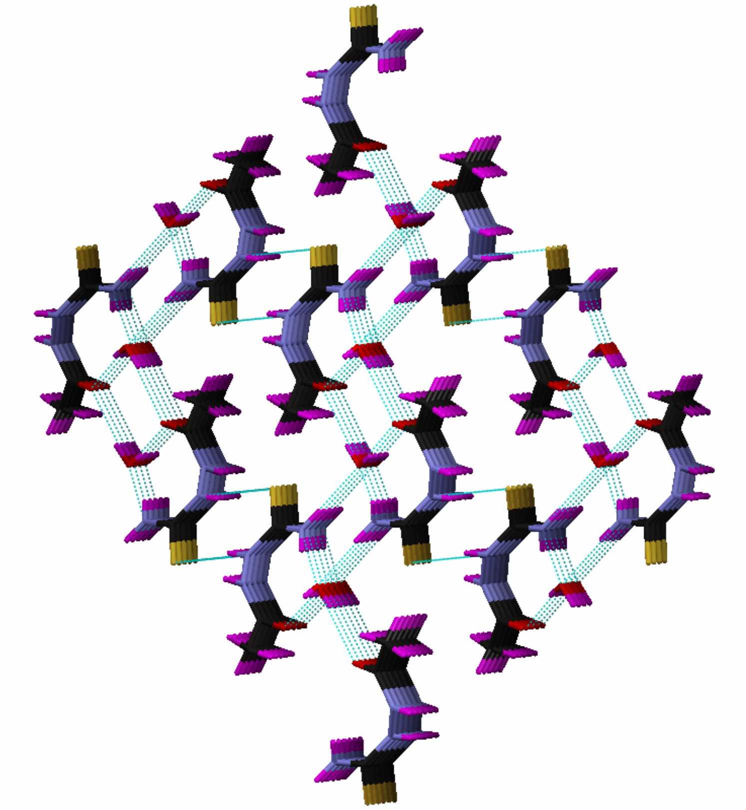


Figure 3: Crystal structure of 1-acetyl-3-thiosemicarbazide and water molecule showing hydrogen bond interactions (network along *b* axis)

Conclusion

X-ray analysis and LC-MS studies reveal that 1-acetyl-3-thiosemicarbazide exists as a monohydrated molecule. X-ray diffraction analysis reveals the presence of four varieties of hydrogen bonding in the crystal packing. The weak hydrogen bonding interactions with zigzag network along with the strong hydrogen bonding interactions form the final 3D structure.

Supplementary material

Crystallographic data (excluding structure factors) for the reported structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 636947. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

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