


Synthesis and crystal structure of *N,N*-dimethylformamide solvate of thiocyanuric acid

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Received: 21 May 2017 / Accepted: 7 November 2017 / Published online: 21 November 2017
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Abstract Considerable attention has been paid recently to crystal engineering; which involves the design and preparation of new crystalline molecular solids with desired properties [1–4]. Crystalline materials with specific properties find applications in petrochemical industry for separation and purification. Moreover, crystal engineering provides products designed for manufacturing catalysts and high-valued chemicals for specific purposes. Recently, crystalline materials find application in pharmaceutical, food and microelectronic industries [5]. The main two strategies that are used for crystal engineering are based on hydrogen bonding and coordination bonding [6]. Since the hydrogen bonding is usually stronger and more directional than the other methods, more new crystal materials have been prepared based on this method. We

are here able to design crystalline materials based on hydrogen bonding and study their solid state structures. *N,N*-dimethylformamide (DMF)-solvate of thiocyanuric acid (TCUA) and dimethyl sulfoxide (DMSO)-solvate of thiocyanuric acid (TCUA) were successfully prepared at room temperature in the presence of aqueous solution of sodium nitrate (NaNO₃). To the best of our knowledge, this study presents the easy, modest, and rapid method to prepare co-crystal formation based on thiocyanuric acid (TCUA) and solvent-containing hydrogen bonding functionality. In this paper, we present the most effective method to synthesize the co-crystals of (TCUA), and as evidence, the crystal structure of (TCUA) in DMF is fully studied and presented in this paper. The *N,N*-dimethylformamide (DMF)-solvate of thiocyanuric acid (TCUA) was successfully prepared at room temperature, and was characterized spectroscopically by nuclear magnetic resonance (NMR) and single-crystal X-ray diffraction (SXRD). The asymmetric unit of the title compound contains one molecule of thiocyanuric acid (TCUA) features an almost planar six-membered ring having exocyclic C-S thione double bonds and one molecule of *N,N*-dimethylformamide (DMF). It was crystallized in the monoclinic, *P2₁/c* with unit cell parameters of $a = 9.6255$ (4) Å, $b = 12.6864$ (5) Å, $c = 9.1367$ (4) Å, $\beta = 90.095$ (2)°, $V = 1115.71$ (8) Å³, $Z = 4$. The structure is composed of 1-D TCUA ribbons formed via N–H–S hydrogen bonds. The ribbons are separated by DMF molecules, which are bridged to the ribbons by N–H–O hydrogen bonds. The ribbons and their DMF molecules form 2-D sheets which are in turn π -stacked to build up a layered, 3-D structure. The proton and carbon-13 NMR studies confirmed the formation of such solvate between DMF and TCUA.

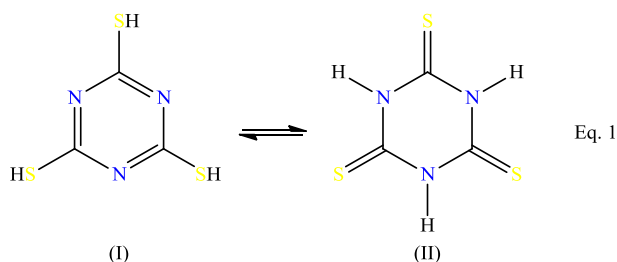
Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13203-017-0191-4>) contains supplementary material, which is available to authorized users.

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Introduction

Thiocyanuric acid (TCUA) is a tribasic, weak acid with acid first, second, and third dissociation constants of 1.99×10^{-6} , 3.98×10^{-9} , and 3.98×10^{-12} , respectively. This polyprotic nature of TCUA permits different degree of deprotonation, and hence, various forms of thiolate and amide ligands for metals and TCUA salts. It is a planar, highly symmetric molecule (D_{3h} point group) and exists as two tautomers: the trithiol form (I) and the trithione form (II), as illustrated in Eq. (1) [7–9]:



1

Each tautomer has three hydrogen bond donor and three hydrogen acceptors at its nitrogen and sulfur atoms. This unique feature enables TCUA to construct self-assembled, supramolecular 1-D chain and 2-D porous structures based on hydrogen bonding [7–21]. The trithiol form (I) is predominant in metal complexes [8–11, 15], whereas the trithione form (II) has been observed to exist in the monolithiated hexamethylphosphoramide complex and in the ammonium salts and solvent adducts of TCUA [7, 8, 12–14, 16–18, 22]. For instance, the triethylammonium salt of TCUA has two polymorphs with 1-D chain structures based on N–H–S and N–H–N hydrogen bonds [16, 23]. On the other hand, the tripropylammonium salt of TCUA has a 2-D structure stabilized by N–H–S and N–H–N hydrogen bonds. The adduct between melamine and TCUA adopts 2-D porous sheets based on planar hexamers connected by N–H–S and N–H–N hydrogen bonds. The melamine/TCUA sheets are stacked to form a 3-D channeled, layered structure [14]. The adduct of 4,4'-bipyridine with TCUA is also constructed by 2-D porous sheets layered into 3-D channeled network, where N–H–S and N–H–N hydrogen bonds are responsible for the self-assembly of 4,4'-bipyridine and TCUA into 2-D sheets [12]. The acetone-solvate of TCUA, [(TCUA)₂(Me₂CO)], is made of 2-D, pseudo-hexagonal planar net, generated by three pairs of N–H–S hydrogen bonds without involvement of acetone in hydrogen bonding. The acetone molecules are hydrogen bonded to hexagons by N–H–O bonds. The acetone molecules also act as pillars between the hexagon layers and result in 3-D channeled network, where the channel

cavity are capped by acetone methyl groups [7, 12]. On the other hand, the methanol solvate of TCUA, [(TCUA)₃(MeOH)], is composed of 1-D, zigzag chains of TCUA via two pairs of N–H–S hydrogen bonds. The TCUA chains are crossed by C–H–S and S–S interactions and are, at the same time, separated by methanol molecules which are also hydrogen bonded with each other and hydrogen bonded to TCUA molecules via N–H–O bonds, generating a 3-D hydrogen-bonded network [7].

We report in this paper the crystal structure of *N,N*-dimethylformamide (DMF) solvate of TCUA, which was discovered accidentally during our attempt to prepare covalent organic framework (COF) of TCUA through the oxidation of thiol functional groups to disulfide functional groups in DMF using a mild oxidant of sodium nitrate at room temperature.

Experimental

Materials

Thiocyanuric acid (TCUA, C₃H₃N₃S₃, > 98.0%, TCI), sodium nitrate (NaNO₃, ReagentPlus, ≥ 99.0%, Sigma-Aldrich), *N,N*-dimethylformamide (DMF, HPLC, ≥ 99.9%, Sigma-Aldrich) were commercially available and were used without further purification. Ultrapure deionized water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

Synthesis procedure

The synthesis of DMF solvate of TCUA (RA5403) was carried out by combining a solution of TCUA (21.27 mg) in DMF (2.0 mL) with an aqueous solution of NaNO₃ (2.0 mL, 1.0 M). The reaction solution was left at room temperature for 3 days, whereupon yellow crystals of RA5403 were obtained. The resulting crystals were filtered off and were washed three times with DMF/water (1:1 v/v). The needle-shaped crystals were obtained in 91% yield.

Analytical and physical characterizations

Proton (600 MHz) and carbon (150 MHz) nuclear magnetic resonance spectra were taken using JEOL ECA-600 Spectrometer. All chemical shifts were referenced to the residual solvent protons/carbons of the solvent indicated. ¹H NMR (600 MHz, DMSO-*d*₆, δ) 7.94 (s, 1H), 2.88 (s, 3H), 2.72 (d, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ) 171.87, 162.32, 35.81, 30.79.

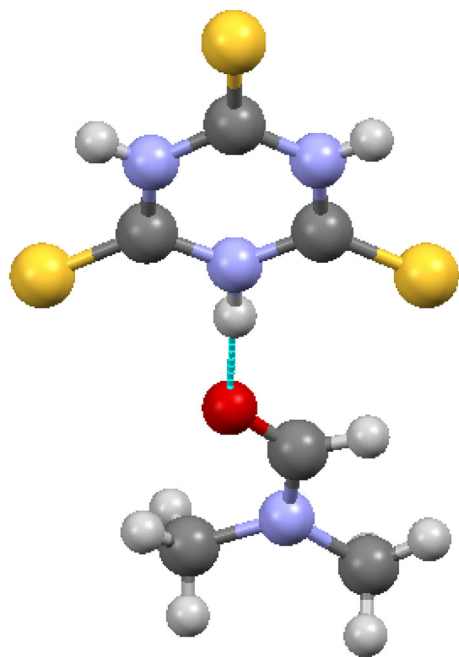


Fig. 1 Asymmetric unit of DMF solvate of TCUA (viewed along a-axis); yellow: sulphur, red: oxygen; sky blue: nitrogen, grey: carbon, white: hydrogen, dashed line: H-bond

X-ray crystallography

Data were collected on a Bruker APEX-II D8 Venture area diffractometer, equipped with graphite monochromatic Mo K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$ at 100 (2) K. Cell refinement and data reduction were carried out by Bruker SAINT. SHELXT [13, 14] was used to solve structure. The final refinement was carried out by full-matrix least-squares techniques with anisotropic thermal data for nonhydrogen atoms on F. CCDC 1455209 contains the supplementary crystallographic data for this compound, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Discussion

Thiocyanuric acid (TCUA) is very well known to form polymers through extensive hydrogen bonds [7, 8, 16, 18, 24]. Here, we were able to prepare a layered, 3D-structure of TCUA with DMF, where the TCUA molecule N–H bonds act as H-bond donors and TCUA molecule C–S bonds and DMF molecule C=O bonds serve as H-bond acceptors. The crystal structure of DMF-solvate of TCUA, reported herein, revealed that TCUA adopts the trithion form (II, Eq. 1). The asymmetric unit of the DMF solvate of TCUA is based on a hydrogen bond (N–H–O) bridge connecting a TCUA molecule and a DFM molecule

Table 1 Experimental details

Crystal data	
Chemical formula	$C_3H_3N_3S_3 \cdot C_3H_7NO$
Mr	250.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.6255 (4), 12.6864 (5), 9.1367 (4)
β (°)	90.095 (2)
V (Å ³)	1115.71 (8)
Z	4
Radiation type	Mo K_{α}
μ (mm ⁻¹)	0.64
Crystal size (mm)	0.52 × 0.41 × 0.06
Data collection	
Diffractometer	Bruker APEX-II D8 venture diffractometer
Absorption correction	Multi-scan SADABS Bruker 2014
Tmin, Tmax	0.731, 0.962
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26745, 4448, 3069
R_{int}	0.052
Refinement	
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.036, 0.090, 1.02
No. of reflections	4448
No. of parameters	145
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.41, -0.40

Table 2 Selected geometric parameters (Å, °)

S1–C1	1.6550 (12)	N2–C2	1.3675 (15)
S2–C2	1.6476 (13)	N3–C1	1.3662 (15)
S3–C3	1.6570 (12)	N3–C3	1.3658 (15)
O1–C6	1.2405 (16)	N4–C4	1.4590 (17)
N1–C1	1.3674 (16)	N4–C5	1.4592 (16)
C1–N1–C2	125.22 (10)	S1–C1–N3	122.56 (9)
C2–N2–C3	125.15 (10)	S2–C2–N2	123.07 (8)
C1–N3–C3	124.08 (10)	N1–C2–N2	114.36 (11)
C4–N4–C6	122.01 (11)	S2–C2–N1	122.57 (8)
C4–N4–C5	118.03 (10)	N2–C3–N3	115.64 (10)
C5–N4–C6	119.96 (11)	S3–C3–N2	122.20 (9)

solvent, as shown below in Fig. 1. The crystallographic data and refinement information are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2. The asymmetric unit is containing of one

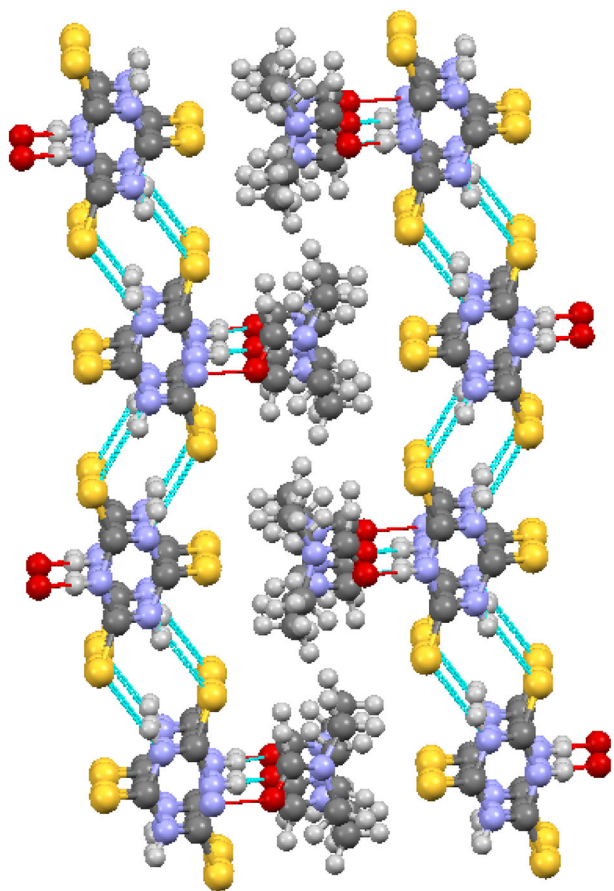
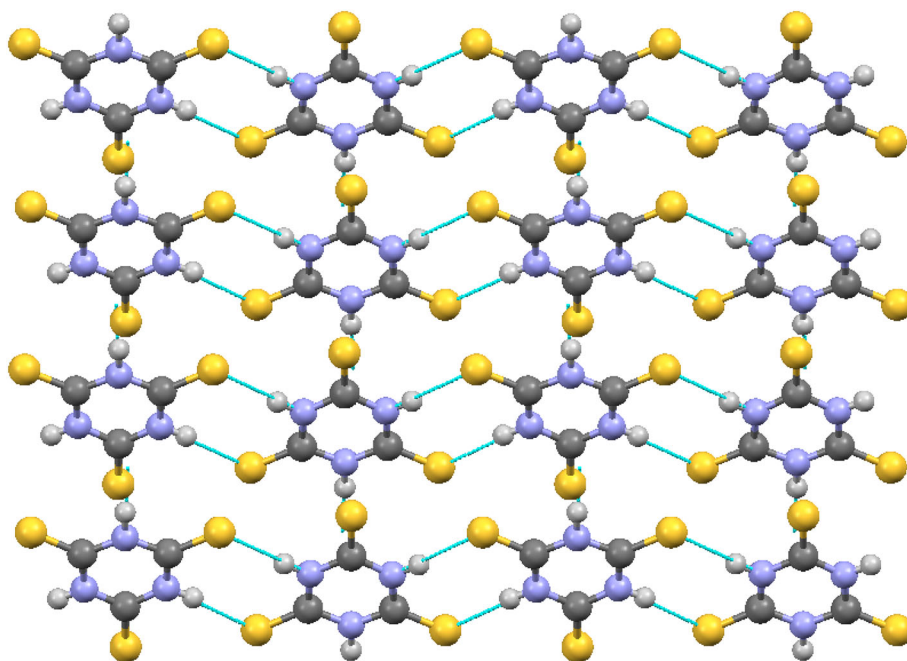


Fig. 2 The crystal structure packing of hydrogen-bonded TCUA ribbons which are hydrogen bonded to DMF molecules forming a 2-D sheets, where these sheets are turned form a layered, 3-D structure (viewed along *c*-axis); yellow: sulphur, red: oxygen; sky blue: nitrogen, grey: carbon, white: hydrogen, dashed lines: H-bonds

Fig. 3 The parallel TCUA ribbons in the different sheets held by π stacking (viewed along *a*-axis); yellow: sulphur, sky blue: nitrogen, grey: carbon, white: hydrogen, dashed lines: H-bonds



independent molecule as shown in Fig. 1. All the bond lengths and angles are in normal ranges [25]. In the crystal packing, Figs. 2 and 3, molecules are linked via intermolecular hydrogen bonds (Table 3).

The TCUA molecules form a one-dimensional zigzag ribbons, where the TCUA molecules within each ribbon are bridged by N–H–S hydrogen bonds. The TCUA ribbons are separated by DMF molecules, which are in turn hydrogen bonded to TCUA molecules through N–H–O bridges in an alternative fashion between two TCUA ribbons, as shown in Fig. 2.

The TCUA ribbons along with their H-bonded DMF molecules form a two-dimensional sheet, as shown in Fig. 2. These sheets are in turn paralleled to other sheets through Van der Waals forces (π stacking), converting the 2-D sheets into a layered, three-dimensional structure. Figure 3 shows the TCUA ribbons which are paralleled in the different sheets.

The crystal structure pattern of our DMF solvate of TCUA is similar to those observed previously for triethylammonium thiocyanurate [9], methanol solvate of TCUA [7], tripropylammonium thiocyanurate, and the second polymorph of triethylammonium thiocyanurate [18].

The formation of the DMF solvate of TCUA was also confirmed by both liquid-state proton and carbon-13 NMR investigations. The proton NMR spectrum showed only DMF peaks at (DMSO-*d*₆, δ) 7.94, 2.88, and 2.72 which could be due to the hydrogen bond, N–H–O, formation between DMF and TCUA, reflecting the partial preservation of the DMF solvate of TCUA in the liquid state. On the other hand, carbon-13 NMR spectrum showed both

Table 3 Hydrogen-bond geometry (Å, °)

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1N1...S3 ^a	0.868 (16)	2.452 (16)	3.3037 (11)	167.4 (15)
N3–H1N3...O1	1.02 (2)	1.64 (2)	2.6577 (14)	174 (2)
N2–H1N2...S1 ^b	0.858 (15)	2.473 (15)	3.3125 (11)	166.5 (14)

Symmetry codes: ^a $-x + 1, y - 1/2, -z + 1/2$ ^b $-x + 1, y + 1/2, -z + 1/2$

TCUA and DMF carbons at (DMSO-6, δ) 171.87, 162.32, 35.81, 30.79.

Conclusion

We prepared readily a layered, 3-D DMF solvate of TCUA at room temperature in the presence of a mild oxidant of NaNO₃. The unsuccessful attempt for synthesizing a COF via oxidizing the TCUA thiol functional groups into disulphide functional groups could be attributed to the thermodynamic preference of TCUA to adopt the trithione form; and the probability need for harsher conditions of temperature, pressure, and oxidation. The structure of DMF solvate of TCUA was studied by SXRD. The NMR studies confirmed the formation of this solvate (see the supporting info).

Acknowledgements This work was sponsored by King Abdulaziz City for Science and Technology (KACST), Saudi Arabia (Grant No. 20-0044).

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