

КРАТКИЕ СООБЩЕНИЯ

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MOLECULAR AND CRYSTAL STRUCTURES OF *bis*-TETRAZOLATE AMMONIUM SALT AND *bis*-TETRAZOLE MONOHYDRATE

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The title compounds *bis*-tetrazolate ammonium salt (**I**) and *bis*-tetrazole monohydrate (**II**) are synthesized and studied by single crystal and powder X-ray diffraction, IR and elemental analyses. Compound **I** crystallizes in the monoclinic space group $C2/m$, $a = 8.8862(17) \text{ \AA}$, $b = 11.2334(21) \text{ \AA}$, $c = 3.7269(7) \text{ \AA}$, $\beta = 99.4(6)^\circ$, $V = 367.03 \text{ \AA}^3$ (12), $Z = 2$. Compound **II** crystallizes in the monoclinic space group $P2_1/c$, $a = 5.1701(9) \text{ \AA}$, $b = 4.7506(8) \text{ \AA}$, $c = 15.2197(24) \text{ \AA}$, $\beta = 107.2(7)^\circ$, $V = 357.09(10) \text{ \AA}^3$, $Z = 2$. In the structure of **I**, both ammonium cation and *bis*-tetrazolate counter-anion are located on twofold crystallographic axes, moreover, the *bis*-tetrazolate anion has a mirror plane passing through the C1—C1a bond. In the crystal structure of (**II**), the *bis*-tetrazole molecule sits on the twofold axis (bisecting the C1—C1a bond), whereas the solvent water molecule occupies a general position. In the crystal structure of (**I**), the molecules are packed via N—H...N intermolecular interactions. In the crystal structure of (**II**), the molecules are packed via N—H...O and O—H...O intermolecular interactions. In addition, the crystal packing of both structures is further strengthened by π — π stacking interactions.

Keywords: crystal structure, *bis*-tetrazole, X-ray diffraction, hydrogen bonding.

Introduction. Tetrazoles are an important class of heterocycles in a wide range of applications, such as catalysis, explosives, propellants and in medicinal chemistry [1—3]. Derivatives of tetrazoles are attractive as gas-generating agents [4, 5] in automobile air bags due to their endothermicity and a high nitrogen content (80 %) and also relative stability of the tetrazole heterocycle.

These nitrogen rich compounds have many electronegative atoms available for the hydrogen bonding and azole (in particular, tetrazole) based energetic materials have attracted considerable attention [6, 7] since they tend to show a good compromise between a high energy content and high thermal stability with low sensitivity [8]. Though the structure of 5,5'-bitetrazole has been solved [9], its ammonium salt and parent monohydrate structures have not been reported. Keeping in view the importance of these azole based materials, we have synthesized the title molecules and present herein the crystal structures obtained by the single crystal X-ray diffraction technique.

Experimental. Materials and physical measurements. All materials and reagents were obtained commercially and used without purification. The elemental analyses of C, H, N and O were carried out using an American PE2400 II CHNS/O elemental analyzer. IR spectra were recorded on a Thermo Nicolet Nexus-670 FT-IR spectrophotometer in the region 4000—400 cm^{-1} as KBr pellets. Powder X-ray diffraction patterns were recorded at room temperature on a Bruker-AXS D8-Advance, X-ray diffractometer with graphite-monochromated $\text{CuK}\alpha$ radiation (1.5406 \AA) and 2θ ranging from 5° to 50° with a step size of 0.005° and a step time of 13.5 s. The diffractometer is attached with high sensitive Lynx-Eye detector.

CAUTION! In general tetrazole derivatives are very sensitive and powerful explosives, sensitive to friction, shock and fast heating, readily attack metals forming explosive salts. Although we had no problems in the synthesis, the work with these compounds should be done with great care and proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs).

Synthesis of the title compounds. Crystals of compound **I** were obtained by dissolving 2 mmol of **I** in 20 ml of distilled water and methanol (1:1). Few drops of 0.1N ammonia solution were added to it and the mixture was stirred for 30 min. On slow evaporation transparent colorless crystals were obtained after 3 days. Anal. calcd. for (**I**), C₂H₈N₁₀ (%): C, 13.95; H, 4.65; N, 81.39. Found (%): C, 13.90; H, 4.59; N, 81.47.

For compound **II**, the above process was repeated without an ammonia solution. Crystals of colorless blocks were obtained after 4 days. Anal. calcd. For (**II**), C₂H₆N₈O₂ (%): C, 15.19; H, 3.80; N, 70.89; O, 10.13. Found (%): C, 15.24; H, 3.73; N, 70.82; O, 10.20.

X-ray diffraction analysis. Single crystal X-ray diffraction data were measured at room temperature with a Bruker SMART Apex CCD area detector [10]. Preliminary lattice parameters and orientation matrix were obtained from three sets of frames. Intensity data were collected using graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$).

Integration and scaling of the intensity data were accomplished using SAINT [10]. The structure was solved by direct methods and refined by a full matrix least-squares procedure based on F^2 [11]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in calculated positions in the riding model approximation. The details of the data collection and refinement are summarized in Table 1. The geometry and molecular graphics were computed using PARST [12], ORTEP-3 [13], and PLATON [14] programs.

Table 1

Crystallographic data and data collection parameters

Parameters	I	II
Empirical formula	2(CN ₄) ⁻ · 2(NH ₄) ⁺	C ₂ H ₂ N ₈ · 2(H ₂ O)
Formula weight	172.18	174.12
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>P2₁/c</i>
Unit cell dimensions, Å, deg.	<i>a</i> 8.8862(17), <i>b</i> 11.2334(21) <i>c</i> 3.7269(7), β 99.4(6)	<i>a</i> 5.1701(9), <i>b</i> 4.7506(8) <i>c</i> 15.2197(24), β 107.2(7)
<i>V</i> , Å ³	367.03(12)	357.09(10)
<i>Z</i>	2	2
<i>D</i> _{cal} , Mg/m ³	1.558	1.619
μ , mm ⁻¹	1.221	1.392
Radiation (MoK _α), Å	0.71073	0.71073
<i>F</i> (000)	180.0	180
θ range for data collection, deg.	2.95—24.95	2.80—24.99
Reflections collected / independent	1581 / 325	3122 / 633
No. of reflections [<i>I</i> > 2 σ (<i>I</i>)]	306	616
No. of parameters	38	68
Final <i>R</i> indices <i>R</i> / <i>wR</i>	0.0363 / 0.0907	0.0335 / 0.0833
Goodness of fit on F^2	1.152	1.160
Refinement method	Full-matrix least-squares on F^2	Full-matrix l. s. on F^2
Measurement	Bruker SMART CCD	Bruker SMART CCD
Program system	SAINT	SAINT
Structure determination / refinement	SHELXS97 / SHELXL97	SHELXS97 / SHELXL97
Molecular graphics	ORTEP-3 and PLATON	ORTEP-3 and PLATON

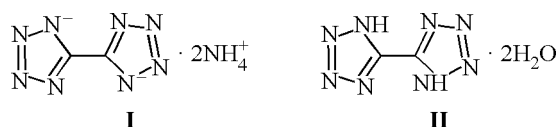
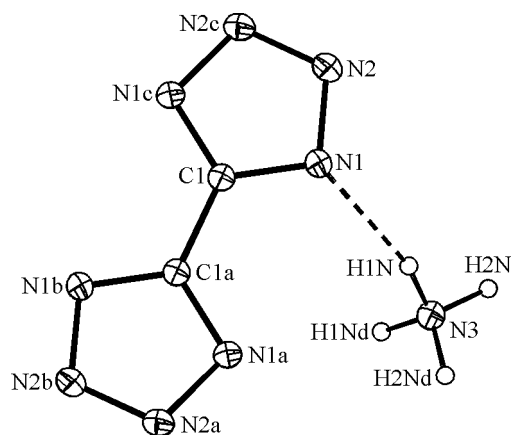
Schematic diagram of the molecule of **I** and **II**

Fig. 1 (right). ORTEP drawing of **I** showing the atom numbering scheme.

Thermal ellipsoids are drawn at 30% probability level. Dashed line denotes the intramolecular hydrogen bond



The structural data for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre under the number CCDC 909593-909594. CIF files containing complete information on the studied structures may be obtained free of charge from the Director, CCDC, 12, Union road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or from the following web site http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. IR spectra. The IR spectra of the ligand and its complexes (compounds **I** and **II**) were recorded separately. The IR spectra of the compounds **I** and **II** show few sharp bands in the range 1600—1430 cm^{-1} that may be assigned to $\gamma(\text{N}=\text{N})$ modes of the tetrazole ring. The bands for the C—N stretching vibrations, which normally appear at 1280—1260 cm^{-1} , did not resolve in both compounds. In compounds **I** and **II**, the typical broad complex set of intense bands appeared in the range 3200—2880 cm^{-1} can be ascribed to the $\gamma(\text{N}—\text{H})$ stretching. The medium intense band at 3186 cm^{-1} in (**I**) (3184 cm^{-1} in (**II**)) may correspond to the $\gamma(\text{C}—\text{H})$ stretching vibration. In compound (**II**), a broad and weak intense band at 3452 cm^{-1} indicates the presence of water in the crystal lattice, which is confirmed by the XRD studies. The bands with medium to weak intensities at 700—1350 cm^{-1} (**I** and **II**) are tentatively assigned to $\gamma(\text{N}—\text{C}—\text{N})$ and $\gamma(\text{N}—\text{N})$ of the tetrazole ring [15].

Description of the crystal structure. The asymmetric unit of compound (**I**) contains one quarter of the *bis*-tetrazolate dianion and half of the cation, where the dianionic moiety has a crystallographic twofold and a mirror symmetry and the cationic moiety passes through a twofold axis. In compound **II**, the asymmetric unit contains one half of the *bis*-tetrazole moiety that crystallizes about a center of inversion and the water molecule occupies a general position. A perspective view of **I** and **II** is shown in Figs. 1 and 2. The geometric conformation of the molecule of **I** is close to that of **II**. In **II**, the tetrazole cycle is practically planar (the average torsion angle C1—N4—N3—N2 and C1—N1—N2—N3

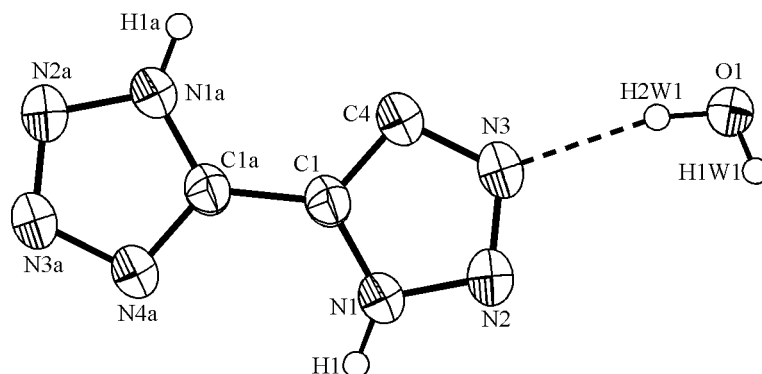


Fig. 2. ORTEP drawing of **II** showing the atom numbering scheme.

Thermal ellipsoids are drawn at 30 % probability level.

Dashed line denotes the intra-molecular hydrogen bond

Table 2

Selected geometric parameters, Å, deg.

Compound I		Compound II			
C1—N1	1.334(2)	C1—N1	1.329(2)	N2—N3	1.295(2)
N1—N2	1.347(2)	N1—N2	1.333(2)	C1—C1a	1.452(2)
C1—C1a	1.464(3)	N3—N4	1.354(1)	N1—C1—N4	109.54(11)
C1—N1—N2	104.43(11)	C1—N4	1.316(2)	C1—N1—N	108.31(10)

Table 3

Hydrogen bonding geometry, Å, deg.

D—H...A	D—H	H...A	D...A	D—H...A
Compound I				
N3—H1N...N	0.91	2.07	2.950(2)	162.2(2)
N3—H2N...N2 ⁱ	0.96	2.00	2.955(2)	177.0(2)
Compound II				
O1W—H2W...N	0.88	1.99	2.849(21)	165.7(2)
N1—H1...O1W ⁱ	0.86	1.83	2.672(2)	169.3(2)
O1W—H1W...O1W ⁱⁱ	0.83	2.96	2.238(24)	146.3(2)

Symmetry code: compound I: (i) $1/2-x, 1/2-y, -z$; compound II: (i) $x+1, y+1, z$; (ii) $-x, y+1/2, -z+3/2$.

is $0.24(2)^\circ$ with a maximum deviation of $0.0018(12)^\circ$ for the N2 atom from the C1,N1—N4 least-squares plane) due to the presence of the center of inversion and the molecule exists in a conformation which is transoid about the inter-ring bond. The relatively short inter-ring bond lengths in both molecules (**I** and **II**) (Table 2) suggests conjugation between the two rings, a feature being common in 5-aryltetrazoles [16]. In **II**, the atomic distances within the ring differ significantly with the shortest bond being between the N2 and N3 atoms ($1.295(2) \text{ \AA}$); they are consistent with the formation of a formal double bond between these atoms. The bond distances between the N—N and C—N single bonds are shorter and the N=N and C=N double bonds are longer than the usual single and double bonds (Table 2). This suggests that there is a considerable delocalization of charge within the ring. Similar results were also found in the literature for other tetrazoles [17—19].

In the crystal structure of **I**, the N1 nitrogen atom of the tetrazolate ring is connected to the ammonium N3 atom via the N—H...N intramolecular hydrogen bond. The molecules are packed using four anionic *bis*-tetrazolates together with four ammonium cations leading to a DAAD type array (D is a hydrogen-bond donor and A is a hydrogen-bond acceptor) of eight hydrogen bonds. The DAAD motif can be represented in the form of $R_8^8(30)$ [20] supramolecular rings (in the *ab* plane) through the N—H...N hydrogen bonding (Table 3). Interestingly, inside these supramolecular rings graph-set $R_4^4(16)$ and $R_8^8(21)$ motifs are contained. Further, each $R_8^8(21)$ motif is surrounded by four $R_4^4(16)$ rings (Fig. 3 shows a part of the supramolecular ring structure). Additionally the structure is stabilized by weak $\pi-\pi$ stacking interactions [21], existing between the tetrazolate rings of two molecules related by the symmetry transformation ($x, -y, 1+z$), with the centroid—centroid distance being $3.727(1) \text{ \AA}$. These interactions further connect the two-dimensional network into a three-dimensional polymeric structure.

In the crystal structure of **II**, the nitrogen atom (N3) in the tetrazole ring and the water molecule are linked through intramolecular O—H...N hydrogen bonds, thereby forming chains of the type C(6)

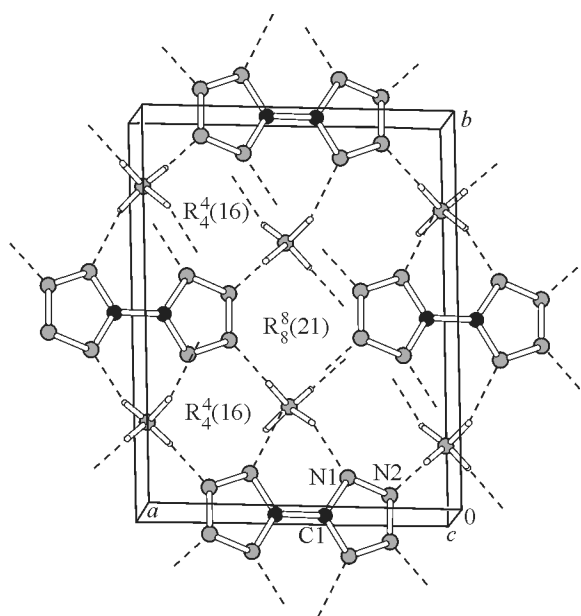


Fig. 3. Fragment of the crystal structure of **I** showing the DAAD array of hydrogen bonds leading to a supramolecular mesh-like structure in the *ab* plane.
Dashed lines indicate hydrogen bonds

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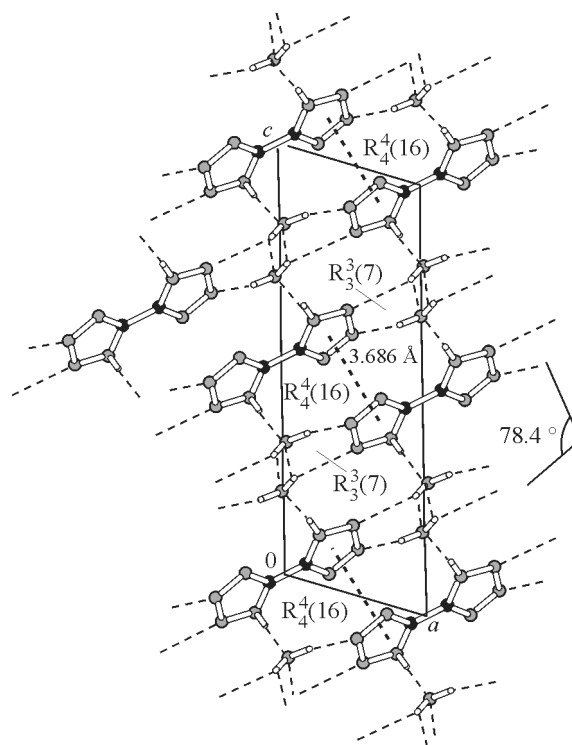


Fig. 4. Part of the crystal structure of **II** showing the formation of a chain of edge-fused $R_3^3(7)$ and $R_4^4(16)$ rings running diagonally in the *ac* plane.
Dashed lines indicate hydrogen bonds

Dashed lines indicate hydrogen bonds

running diagonally in the *ab* plane (Fig. 4). These chains are further connected into supramolecular network along the *c* axis through a combination of N—H...O and O—H...O intermolecular hydrogen bonds to form $R_4^4(16)$ dimers and $R_3^3(7)$ edge-fused rings. In the *ac* plane, the angle between the layers containing the $R_4^4(16)$ and $R_3^3(7)$ motifs is 78.43° . In addition, the crystal packing is further strengthened by π — π stacking interactions through inversion-related tetrazole rings of two molecules (symm: $1-x, 1-y, -z$) with the centroid—centroid distance being $3.686(1) \text{ \AA}$ (Table 3).

Powder XRD measurement. The simulated and experimental powder X-ray diffraction patterns of *bis*-tetrazolate ammonium salt **I** and *bis*-tetrazole monohydrate **II** (Figs. 5 and 6) are in good

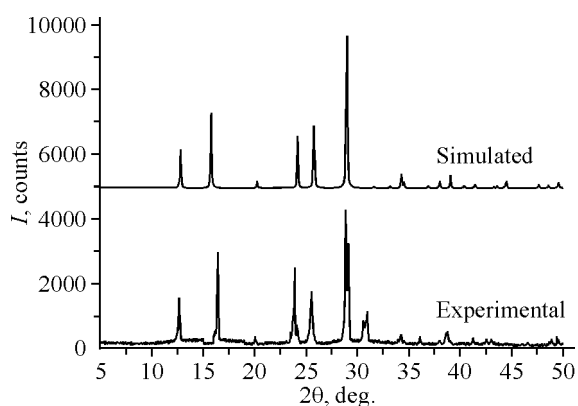


Fig. 5. Simulated and experimental PXR patterns of *bis*-tetrazolate ammonium salt **I**

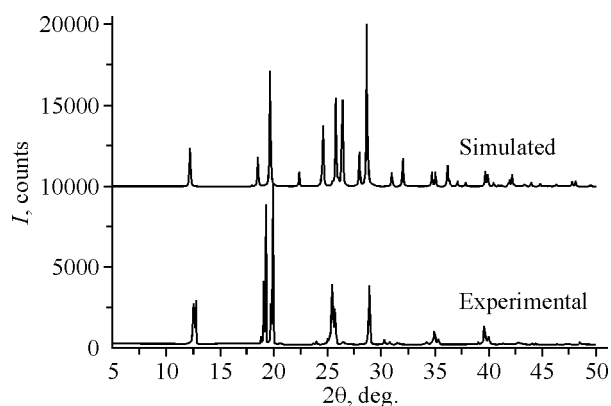


Fig. 6. Simulated and experimental PXR patterns of *bis*-tetrazolate monohydrate **II**

agreement with each other. A few additional peaks and some differences in the intensities between the peaks of the patterns were found. This may be attributed to a very minor quantity of an impurity phase and the effect of the preferred orientation of the powder sample.

In summary, the crystallographic characterization of two *bis*-tetrazole derivatives **I** and **II** are reported.

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