

# CHN<sub>7</sub> – A Molecule Like Almost Solid Nitrogen

By

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## Abstract

In this communication, we present the crystal structure of an energetic salt – a dysprosium 5,5'-azotetrazolate hydrate with a 5-azido-2*H*-tetrazole adduct and, thereby, the first complete crystal structure of a 5-azidotetrazole molecule (CHN<sub>7</sub>). Furthermore, it is the first structural evidence for a 2*H*-tautomer of this molecule: By careful analysis of the hydrogen bonding in the crystal, we could unambiguously locate the hydrogen atom at the N2 position. The extremely sensitive and energetic 5-azidotetrazole presented herein is the nitrogen-richest organic molecule which has ever been completely structurally characterized. The dysprosium compound is the first co-crystal of a 5,5'-azotetrazolate anion with a neutral 5-substituted tetrazole derivative adduct. It is also the first structurally characterized azotetrazolate of an f-block element. Our result shows that 5-azido-2*H*-tetrazole is the product of Lewis acidic decomposition of 5,5'-azotetrazole in water in presence of nitrate.

## 1. Introduction

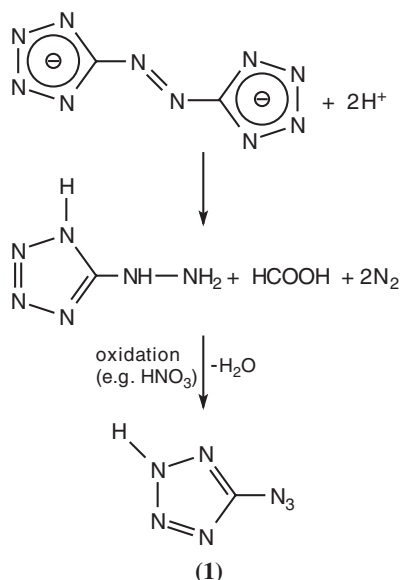
Tetrazoles are unsaturated 5-membered aromatic heterocycles containing four nitrogen atoms. The nitrogen content of the unsubstituted CH<sub>2</sub>N<sub>4</sub> molecule is almost 80%. Derivatives of tetrazole are object of recent preparative chemical research [1] and promising materials for many applications as energetic materials [2, 3]. 5-Azidotetrazole (CHN<sub>4</sub>N<sub>3</sub>, **1**) has long been an object of investigation because of its extremely high nitrogen content (88.3%) [4, 5] and for application as a

potential primary explosive [6–8]. However, THIELE and INGLE concluded from their investigations on **1** more than 110 years ago that due to its highly sensitive character, “a direct analysis of the nitrogen-richest compound among organic molecules is absolutely impossible” [4].

In a theoretical study, the 5-azido-2*H*-tetrazole was calculated to be more stable than the corresponding 1*H*-isomer [9]. Thus it was somewhat surprising that in an earlier determination of the crystal structure of pure **1** [10], the tetrazole ring was found to be protonated on the N1 position. The fits, wR2, R1 etc. of the crystal structure of 5-azido-1*H*-tetrazole in that [10] paper are of relatively poor quality and thus left many questions open. Those authors used the reaction of 5-aminotetrazole, sodium nitrite and hydrochloric acid to form the tetrazole diazononium chloride. This compound was reacted with sodium azide and formed **1** under loss of dinitrogen.

Furthermore, **1** has been reported to form as a byproduct of the acidic decomposition of the 5,5'-azotetrazolate (ZT) under oxidizing conditions (see Scheme 1) [11–13].

The final reaction products of the degradation of 5,5'-azotetrazolate with nitric acid are 5-azido-2*H*-tetrazole, dinitrogen, carbon dioxide and dinitrogen monoxide, as shown in [14].

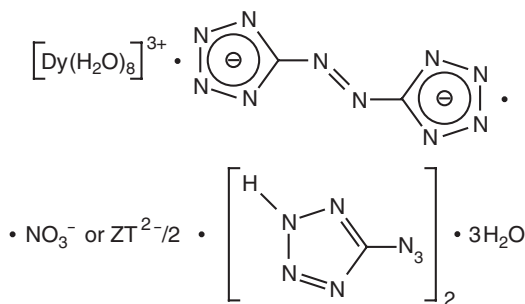


Scheme 1. Acidic decomposition of 5,5'-azotetrazolate and formation of **1** in aqueous media

Infrared spectroscopy readily identifies **1** by the antisymmetric stretching vibration of the azido group [15–17]. In a paper on several mono-, di- and trivalent metal salts of 5,5'-azotetrazolate, IR data have been tabulated [18]. Interestingly, only the lanthanide compounds investigated in that study (La<sub>2</sub>ZT<sub>3</sub>, Ce<sub>2</sub>ZT<sub>3</sub>, Nd<sub>2</sub>ZT<sub>3</sub>, Gd<sub>2</sub>ZT<sub>3</sub>) show the typical IR band of a covalent azide. For the cerium(III) ZT, the typical IR band around 2150 cm<sup>-1</sup> is not listed in that paper. Close inspection of the original IR spectra clearly shows this peak as well. In that paper, the possible existence of an azide – most likely 5-azido-tetrazole – as an impurity in the respective lanthanide 5,5'-azotetrazolate salts is not discussed.

## 2. Results and Discussion

Herein, we would like to communicate a highly interesting result to the Austrian Academy of Sciences: the structurally characterized product of the reaction of sodium 5,5'-azotetrazolate and dysprosium trinitrate in water – the unusual high-nitrogen compound octaaquadydysprosium(III)–5,5'-azotetrazolate–nitrate (or ZT/2)–5-azido-2*H*-tetrazole–water (1/1/1/2/3 or 4) (**2**) and, thereby, the first structural characterization of a 5-azido-2*H*-tetrazole molecule (see Table 1).



(2)

Dysprosium trinitrate supports the formation of 5-azidotetrazole in several ways. Due to the lanthanide contraction, the Dy<sup>3+</sup> ion is more acidic than, e.g. La<sup>3+</sup> or Gd<sup>3+</sup> and thus enhances the decomposition of 5,5'-azotetrazolate. Furthermore, as a member of the heavier “yttric earths”, its basic salts are characterized by a higher solubility and thus reactivity than the respective basic salts of the “cerite earths” [19]. Lastly, nitrate is known to oxidize the 5-hydrazinetetrazole forming the azide in acidic solution, eventually after reduction to nitrite [11, 12, 14].

Table 1. Crystal structure and refinement data of **2** (assuming the presence of  $\text{NO}_3^-$ )

Empirical formula	$\text{C}_4\text{H}_{24}\text{DyN}_{25}\text{O}_{14}$
Formula weight/g mol <sup>-1</sup>	808.90
Temperature/K	100
Crystal size/mm	0.24 × 0.08 × 0.03
Crystal system	triclinic
Space group	$P\bar{1}$
$a/\text{Å}$	7.2443(7)
$b/\text{Å}$	11.6124(19)
$c/\text{Å}$	19.456(2)
$\alpha/^\circ$	90.428(9)
$\beta/^\circ$	100.141(7)
$\gamma/^\circ$	104.595(11)
$V/\text{Å}^3$	1556.8(3)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.5933(3)
$\mu$ ( $\text{MoK}\alpha$ )/mm <sup>-1</sup>	2.478 ( $\lambda = 0.71073 \text{ Å}$ )
$F(000)$	3.72–28.81
Reflections collected	10690
Reflections unique	8133 ( $R_{\text{int}} = 0.0330$ )
Observed reflections	5007 [ $I > 2\sigma(I)$ ]
$R1$ ( $2\sigma$ )	0.0289
$R1$ (all data)	0.0369
$wR2$ ( $2\sigma$ )	0.0714
$wR2$ (all data)	0.0740
Data to parameter ratio	13.3:1 [ $11.0:1 I > 2\sigma(I)$ ]
GOOF on $F^2$	1.054

Structure solution was performed with SIR-97 [20] with direct methods. Satisfactory atomic positions of the second anion could not reliably be determined. Due to this disorder in the crystal structure, we were not able to clarify the nature of the second anion, it could be nitrate or 5,5'-azotetrazolate. However, the disordered molecules were treated as a diffuse contribution using the program SQUEEZE [21, 22]. SQUEEZE calculated  $520 \text{ Å}^3$  void space per unit cell and 63 electrons; 2 molecules of nitrate require 60 electrons per unit cell and one ZT anion requires 82 electrons, respectively. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Centre (CCDC, 12 Unions Road, Cambridge CB21EZ (Fax: (+44)1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk), on quoting the depository number CCDC 670405.

In the molecular structure of **2**, two independent molecules of 5-azido-2*H*-tetrazole (Fig. 1) are present and arranged as staggered

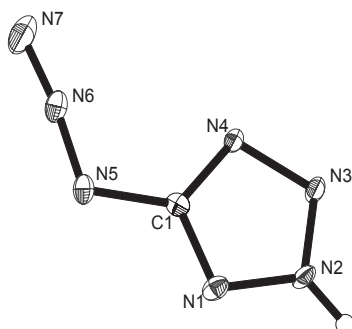


Fig. 1. ORTEP drawing of 5-azido-2*H*-tetrazole in the crystal structure of **2**. Thermal ellipsoids at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.311(5), N1–N2 1.364(5), N2–N3 1.326(6), N3–N4 1.358(5), N4–C1 1.349(5), C1–N5 1.403(5), N5–N6 1.245(5), N6–N7 1.120(6), C1–N5–N6 113.6, N5–N6–N7 172.2(5), C1–N1–N2 102.2(3), N1–N2–N3 110.7(3), N2–N3–N4 109.0(4), N3–N4–C1 102.5(3), N4–C1–N1 115.5(4)

layers along the *a* axis. Due to only marginal differences in the bond distances and bond angles of both molecules, only one of them is discussed in detail. Compound **1** is nearly planar with a slightly shorter terminal N<sub>β</sub>–N<sub>γ</sub> bond length (N6–N7 1.120(6) Å) than the N<sub>α</sub>–N<sub>β</sub> bond length (N5–N6 1.245(5) Å), and an N5–N6–N7 bond angle of 172.2(5)°, which is common for covalent azides [23]. These values, as well as the atom distances in the tetrazole ring, are also in accordance with previously reported experimental data and theoretical predictions [9, 10]; the discrepancy is the different location of the hydrogen atom. Whereas in the published experimental work, the proton is located on the N1 position of the tetrazole ring [10], during our structure refinement, we located the proton at the N2 position in the solid state. 5-Azidotetrazole has been reported to be one of the strongest acids amongst 5-substituted tetrazole derivatives, due to the electron withdrawing properties of the azido-group (pseudohalide) [24]. For 5-substituted tetrazoles with electron withdrawing groups (such as halides (–Cl), pseudohalides (–CN, –CF<sub>3</sub>) or classic electron withdrawing groups, such as –NO<sub>2</sub>, *p*-NO<sub>2</sub>-Ph– or –SO<sub>2</sub>Me) the N2 protonated tautomer is favored in solution, whereas tetrazoles with electron donor substituents in the 5-position such as –NH<sub>2</sub> or –CH<sub>3</sub> are protonated preferentially on N1 [25]. However, due to the minimal energetic differences between both tautomers, it is likely that both can exist, depending on the chemical environment and physical conditions: Temperature and solvent effects also influence the

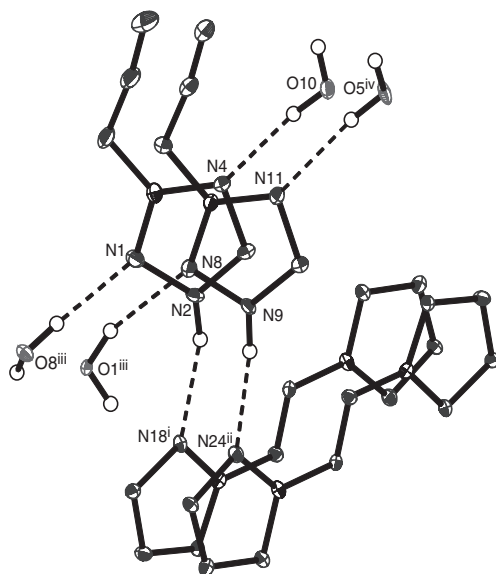


Fig. 2. View of the hydrogen bridges (dashed lines) of the azidotetrazole. Symmetry codes: (i) =  $2 - x, 1 - y, 1 - z$ ; (ii) =  $x, -1 + y, z$ ; (iii) =  $1 - x, -y, 1 - z$ ; (iv) =  $1 - x, 1 - y, 1 - z$

equilibrium between the  $1H$  and  $2H$  tautomers. Our observation of 5-azido- $2H$ -tetrazole in the solid state are not only supported by previous theoretical calculations [9] but also by a careful analysis of the hydrogen bonding in the crystal structure of compound **2**. The hydrogen atom bound to N2 of the tetrazole ring is part of an  $N-H \cdots N$  hydrogen bridge with a donor-acceptor distance of 2.88 Å and an angle of  $170.7^\circ$  with a nitrogen atom of the 5,5'-azotetrazolate moiety (Fig. 2). Both N1 positions are “blocked”, because they are already part of a hydrogen bridge, in this case an  $N \cdots H-O$  bridge to water molecules coordinating the dysprosium cation (donor-acceptor distances 2.83 and 2.90 Å; angles  $161.3$  and  $173.7^\circ$ , respectively).

IR measurements on a small crystal of **2** evidence the existence of a covalent azide (band of the antisymmetric stretching vibration at  $2148 \text{ cm}^{-1}$ ) [see also 16]. Covalent azido moieties show a very poor Raman activity, however, the anion 5,5'-azotetrazolate could be identified by Raman spectroscopy on a small single crystal in its mother liquor.

$^{14}\text{N}$ -NMR measurements were performed with a small amount of the crystals' mother liquor diluted in  $\text{H}_2\text{O}$ . As expected from the

quadrupole moment associated with the nucleus, not all the nitrogen resonances could be observed. The most intense peak corresponds to the resonance of the nitrate anion ( $\delta = +8.9$  ppm), whereas for the azotetrazolate anion just the C–N <sub>$\beta$</sub>  shift is observed at  $\delta = -64.1$  ppm, similarly to other metal azotetrazolates [18]. Lastly, due to the low concentration of the sample, just one peak for the nitrogen resonances of the azide in azidotetrazole **1** is found. This corresponds to the overlap of the azide resonances of the nitrogen atoms crystallographically labelled as N6 and N7 ( $\delta = -126.5$  ppm), which are the most intense peaks in the <sup>14</sup>N-NMR spectrum of previously reported **1** [10]. The rest of the nitrogen resonances corresponding to **1** or the azotetrazolate anion, are much less intense and broader in similar compounds and are thus not observed [26].

### 3. Experimental

**CAUTION!** Azidotetrazole is an extremely sensitive energetic substance and explodes violently upon various stimulation such as heating, impact, friction of electrostatic discharge. The use of safety equipment such as Kevlar<sup>®</sup> gloves, wrist protectors, leather coats, face shields, conducting shoes and ear plugs is mandatory when handling this substance.

Compound **2** formed by the reaction of 133 mg dysprosium(III) nitrate pentahydrate (99.9% provided from the chemical store of the Atominstitut) and 122 mg sodium 5,5'-azotetrazolate pentahydrate (synthesized according to THIELE, see [27]) in aqueous solution. The starting materials were dissolved in 10 mL of water and heated to 90°C for 10 min. A greenish-gray precipitate formed, which did not dissolve by addition of further 10 mL of water. The reaction mixture was cooled in the refrigerator for one hour and the heterogeneous solid residue was removed by filtration. The clear brownish solution was allowed to stand in a closed vial for several months. During that time, small crystals of **2** grew on the bottom of the vial from where they were collected and submitted to X-ray diffraction. We expect to obtain the final distinctiveness on whether nitrate is present in the crystal structure of **2** (or ZT/2 instead) after further investigation (including elemental analysis), which will be performed soon. This does, of course, not affect the fundamental data obtained on the azidotetrazole molecule **1**. Its constitution and configuration presented herein does not leave a doubt on the nature of CHN<sub>7</sub> – a molecule like almost solid nitrogen.

IR <sub>$\bar{\nu}$</sub>  (Diamond-ATR, cm<sup>-1</sup>) = 3340 (vs), 2148 (m), 1634 (s), 1393 (m), 1344 (m), 1106 (w), 726 (sh); Raman (14.5 mW, LabRam HR800

(Horiba Jobin Yvon), 25°C,  $\text{cm}^{-1}$ , rel. intensities in %) 1504 (71), 1485 (24), 1433 (23), 1398 (100), 1107 (43), 1083 (30), 936 (20);  $^{14}\text{N}$ -NMR ( $\text{H}_2\text{O}$ , 20°C)  $\delta/\text{ppm}$ : +8.9 ( $\text{NO}_3^-$ ), -64.1 (azotetrazolate, C-N $_{\beta}$ ), -126.5 (azide, C $_{\beta}$ /C $_{\gamma}$ ).

#### 4. Conclusion

In this study, we determined the first crystal structure of a 5-azido-2*H*-tetrazole, which is the organic molecule with the highest nitrogen content that has ever been completely structurally characterized. In addition, **2** is also the first co-crystal of a 5,5'-azotetrazolate anion with a neutral 5-substituted tetrazole derivative. We could also unambiguously evidence that 5-azidotetrazole is one product of the Lewis acidic decomposition of 5,5'-azotetrazolate by trivalent lanthanoid ions in aqueous solution and in presence of nitrate. Furthermore, **2** is the first structurally characterized f-block element 5,5'-azotetrazolate, our results are also a strong evidence that the 5,5'-azotetrazolate ion does not only decompose in mineral acids but also in a Lewis acidic decomposition of the presented type. *Viribus unitis*.

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