

Article

Crystal Structures of Two 1,4-Diamino-1,2,4-triazolium Salts

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Abstract: Bis(1,4-diamino-1,2,4-triazolium) sulfate (**1**) was obtained from the corresponding chloride by ion metathesis using Ag₂SO₄. Further metathesis with barium 5,5'-azotetrazolate yielded bis(1,4-diamino-1,2,4-triazolium) 5,5'-azotetrazolate (**2**). Numerous NH···N and NH···O interactions were identified in the crystal structures of **1** and **2**. Both compounds undergo exothermal decomposition upon heating.

Keywords: azotetrazolate; hydrogen bond; sulfate; thermoanalysis; triazolium

1. Introduction

N-Aminoazoles are pillars of heterocyclic chemistry, and interest in *N*-aminoazoles and their salts ranges from agrichemistry to medicinal chemistry. In particular, *N,N'*-diaminoazolium salts exhibited attractive biological activities [1]. Thus far, the crystal structure of only one 1,4-diamino-1,2,4-triazolium salt, the chloride, has been published [2]. One of the most exciting developments are nitrogen-rich salts. The synthesis of sodium 5,5'-azotetrazolate was first reported by Thiele [3]. A lot has happened since then in terms of compound synthesis and developments, and a number of salts containing 5,5'-azotetrazolate ions and their crystal structures have been described [4–6]. One can still find small and simple molecules that are neglected in the literature. The 1,4-diamino-1,2,4-triazolium cation is one of those missing links. Bis(1,4-diamino-1,2,4-triazolium) 5,5'-azotetrazolate was reported to spontaneously evolve nitrogen gas and to undergo violent decomposition at 134 °C [7], but no crystal structure was disclosed. Recently, the structure of the closely related bis(1,3-diaminoimidazolium) 5,5'-azotetrazolate was determined [8]. Here, we report the crystal structures of bis(1,4-diamino-1,2,4-triazolium) 5,5'-azotetrazolate and its precursor, bis(1,4-diamino-1,2,4-triazolium) sulfate.

2. Results and Discussion

The synthesis of bis(1,4-diamino-1,2,4-triazolium) sulfate (**1**) was accomplished by metathesis of the corresponding chloride with silver sulfate (Figure 1). In a second metathetical step of the sulfate **1** and barium 5,5'-azotetrazolate, bis(1,4-diamino-1,2,4-triazolium) 5,5'-azotetrazolate (**2**) was obtained. Both steps gave high yields (90% and 98%, respectively). It should be noted that *N*-aminoazoles and *N*-aminoazolium salts which are not derived from hydrazine have to be prepared by electrophilic amination. They are therefore expensive and only of academic interest.

N,N'-Diaminoazolium cations are potent hydrogen bond donors [2,8–10], and it seemed to be of interest to examine the interactions of the 1,4-diamino-1,2,4-triazolium cation with acceptor anions

such as sulfate or 5,5'-azotetrazolate in the solid state. The crystal data and refinement details are summarized in Table 1.

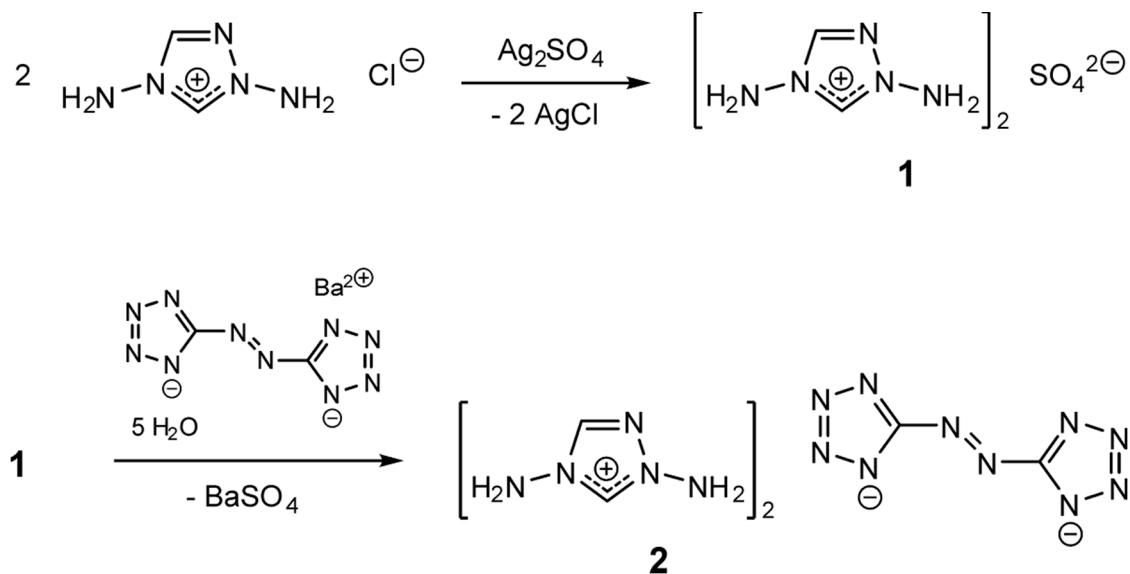


Figure 1. Syntheses of 1,4-diamino-1,2,4-triazolium sulfate (1) and 5,5'-azotetrazolate (2).

Table 1. Crystal data and structure refinement for 1 and 2.

Compound	1	2
CCDC No.	1441522	1441523
Empirical formula	$2(\text{C}_2\text{H}_6\text{N}_5) \cdot \text{O}_4\text{S}$	$2(\text{C}_2\text{H}_6\text{N}_5) \cdot \text{C}_2\text{N}_{10}$
Formula weight	296.30	364.36
Crystal system	Monoclinic	Monoclinic
Space group	Pc	$P2_1/c$
$a/\text{\AA}$	11.0114(3)	3.5735(3)
$b/\text{\AA}$	8.4671(2)	14.8270(12)
$c/\text{\AA}$	12.8156(5)	13.4559(11)
$\beta/^\circ$	92.356(3)	95.664(3)
Volume/ \AA^3	1193.85(6)	709.47(10)
Z	4	2
$D_x/\text{g}\cdot\text{cm}^{-3}$	1.648	1.706
μ/mm^{-1}	0.31	0.13
$F(000)$	616	376
T/K	173	183
Crystal size/ mm^3	$0.54 \times 0.20 \times 0.16$	$0.18 \times 0.04 \times 0.03$
$\theta_{\text{max}}/^\circ$	25.4	25.0
Index ranges	$-13 \leq h \leq 11,$ $-10 \leq k \leq 10,$ $-14 \leq l \leq 15$	$-4 \leq h \leq 3,$ $-17 \leq k \leq 17,$ $-15 \leq l \leq 15$
Reflections collected	7080	9515
Independent reflections (R_{int})	3571 (0.028)	1250 (0.060)
Observed reflections [$I > 2\sigma(I)$]	3428	1001
Absorption correction	multi-scan	multi-scan
Restraints/parameters	18/392	4/135
Goodness-of-fit on F^2	1.09	1.06
R_1/wR_2 [$I > 2\sigma(I)$]	0.026/0.077	0.037/0.092
R_1/wR_2 (all data)	0.029/0.079	0.052/0.098
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}/\text{e}\cdot\text{\AA}^{-3}$	0.23/−0.25	0.54/−0.22

2.1. Bis(1,4-diamino-1,2,4-triazolium) Sulfate (1)

Hydrogen atoms at N3 and N5 were found and refined isotropically. The geometry of the *N*-amino groups was pyramidal, indicating sp^3 hybridization. The *N*-amino group conformations relative to the azolium ring planes were eclipsed (lone pair closely aligned with the ring plane, N–H bonds out of the ring plane), as observed in the structure of the corresponding chloride (Cambridge Structural Database reference code MEBPOZ).

The crystal structure of this simple salt was found to be unexpectedly complicated. There are four independent cations and two anions in the asymmetric unit. Numerous $NH \cdots O$ hydrogen bonds (Table 2) create a three-dimensional framework. These interactions are depicted separately, for the sake of clarity, for each of the four independent cations A–D in Figure 2.

Table 2. Hydrogen bond geometry for 1 and 2 (Å, °).

Compound	Interaction	H...A	D...A	D–H...A	Symmetry Operation A
1	N5 _A –H51 _A ...O5	2.04(2)	2.913(3)	160(3)	x, y, z
	N5 _A –H52 _A ...O3	2.04(2)	2.946(3)	173(3)	x, y, z
	N3 _C –H31 _C ...O1	2.11(3)	3.008(3)	169(3)	x, y, z
	N3 _C –H31 _C ...O3	2.48(3)	3.115(3)	128(3)	x, y, z
	N3 _C –H32 _C ...O5	2.19(3)	2.962(4)	144(3)	$x, -y, -1/2 + z$
	N3 _B –H31 _B ...O2	2.15(2)	2.932(3)	145(3)	$x, 1 + y, z$
	N3 _B –H32 _B ...O7	2.07(2)	2.951(3)	172(3)	$1 + x, y, z$
	N5 _D –H51 _D ...O8	2.06(3)	2.871(3)	151(3)	x, y, z
	N5 _D –H52 _D ...O2	2.16(2)	2.996(3)	155(3)	$-1 + x, y, z$
	N3 _D –H31 _D ...O1	2.00(2)	2.889(3)	163(3)	x, y, z
	N3 _D –H32 _D ...O5	2.16(2)	3.042(4)	170(3)	$x, -1 + y, z$
	N5 _B –H51 _B ...O4	2.14(2)	2.989(4)	162(3)	$x, -y, -1/2 + z$
	N5 _B –H52 _B ...N3 _A	2.26(2)	3.108(4)	159(3)	$x, -y, -1/2 + z$
	N5 _C –H52 _C ...O5	2.11(3)	2.922(4)	152(3)	$x, 1 - y, -1/2 + z$
	N3 _A –H31 _A ...O6	2.03(2)	2.874(3)	157(3)	$1 + x, y, z$
	N3 _A –H32 _A ...O2	1.98(2)	2.856(3)	166(3)	$x, -y, 1/2 + z$
	N3 _B –H32 _B ...O8	2.54(3)	3.123(3)	124(2)	$1 + x, y, z$
	N5 _C –H51 _C ...O1	2.56(3)	3.353(3)	150(3)	$x, 1 + y, z$
	N5 _C –H51 _C ...N3 _D	2.68(3)	3.301(4)	129(2)	$x, 1 + y, z$
2	N10–H _A ...N3	2.12(2)	3.018(2)	169(2)	x, y, z
	N10–H _B ...N1	2.16(2)	3.048(2)	167(2)	$x, 3/2 - y, -1/2 + z$
	N8–H _A ...N2	2.38(2)	3.152(2)	146(2)	$1 - x, 1 - y, 1 - z$
	N8–H _B ...N4	2.64(3)	3.221(2)	125(2)	$-x, -1/2 + y, 1/2 - z$

2.2. Bis(1,4-diamino-1,2,4-triazolium) 5,5'-Azotetrazolate (2)

The salt $(C_2H_6N_5)_2(C_2N_{10})$ consists of 76.9 percent nitrogen and thus can be rightly considered to be “nitrogen-rich.” The hydrogen atoms at N8 and N10 were found and refined isotropically with bond restraints, and the *N*-amino groups again are pyramidal. The ions form cyclic hydrogen-bonded assemblies (Figure 3), which can be described by a $R_2^2(13)$ graph set [11], meaning a 13-membered ring with 2 hydrogen bond donors and 2 acceptors. In contrast, in the structure of the related 1,3-diaminoimidazolium 5,5'-azotetrazolate (CSD reference code YEHTAI) [8] hydrogen bonds between two cations and two anions create centrosymmetric ring-shaped aggregates, graph set $R_4^4(20)$. In 2, a wave-like arrangement of the ions is observed (Figure 3), whereas the very similar salt, 4-amino-1-methyl-1,2,4-triazolium 5,5'-azotetrazolate (CSD reference code PAPMOJ), packed in flat layers and crystallized in an orthorhombic space group [7]. Obviously, the structure of 2 is controlled by the additional hydrogen bonding of the second amino group.

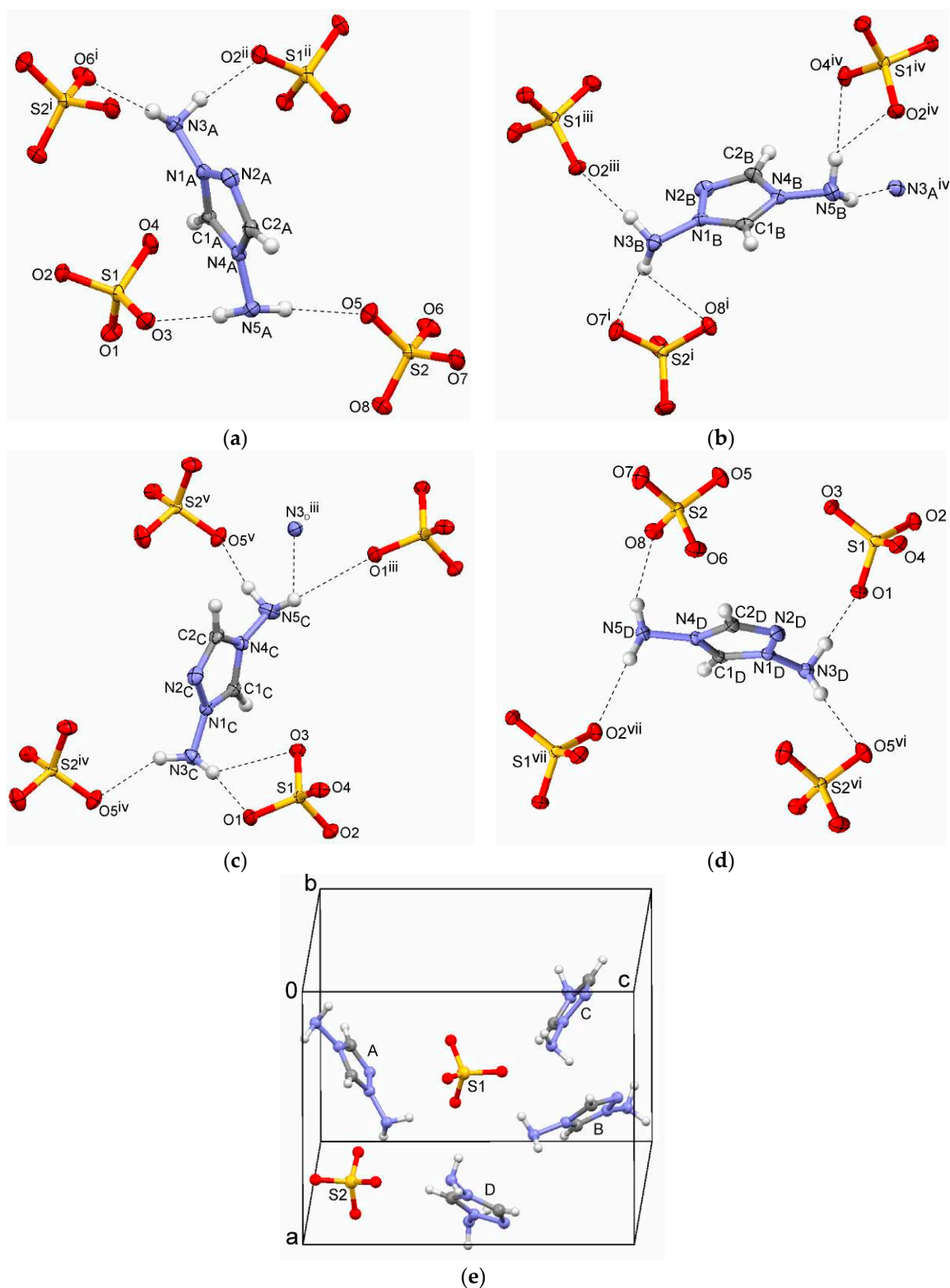


Figure 2. Bis(1,4-diamino-1,2,4-triazolium) sulfate (1). **(a–d)** The four independent cations as hydrogen-bond donors. Symmetry codes: (i) $1+x, y, z$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $x, 1 + y, z$; (iv) $x, -y, -\frac{1}{2} + z$; (v) $x, 1 - y, -\frac{1}{2} + z$; (vi) $x, -1 + y, z$; (vii) $-1 + x, y, z$; **(e)** Asymmetric unit.

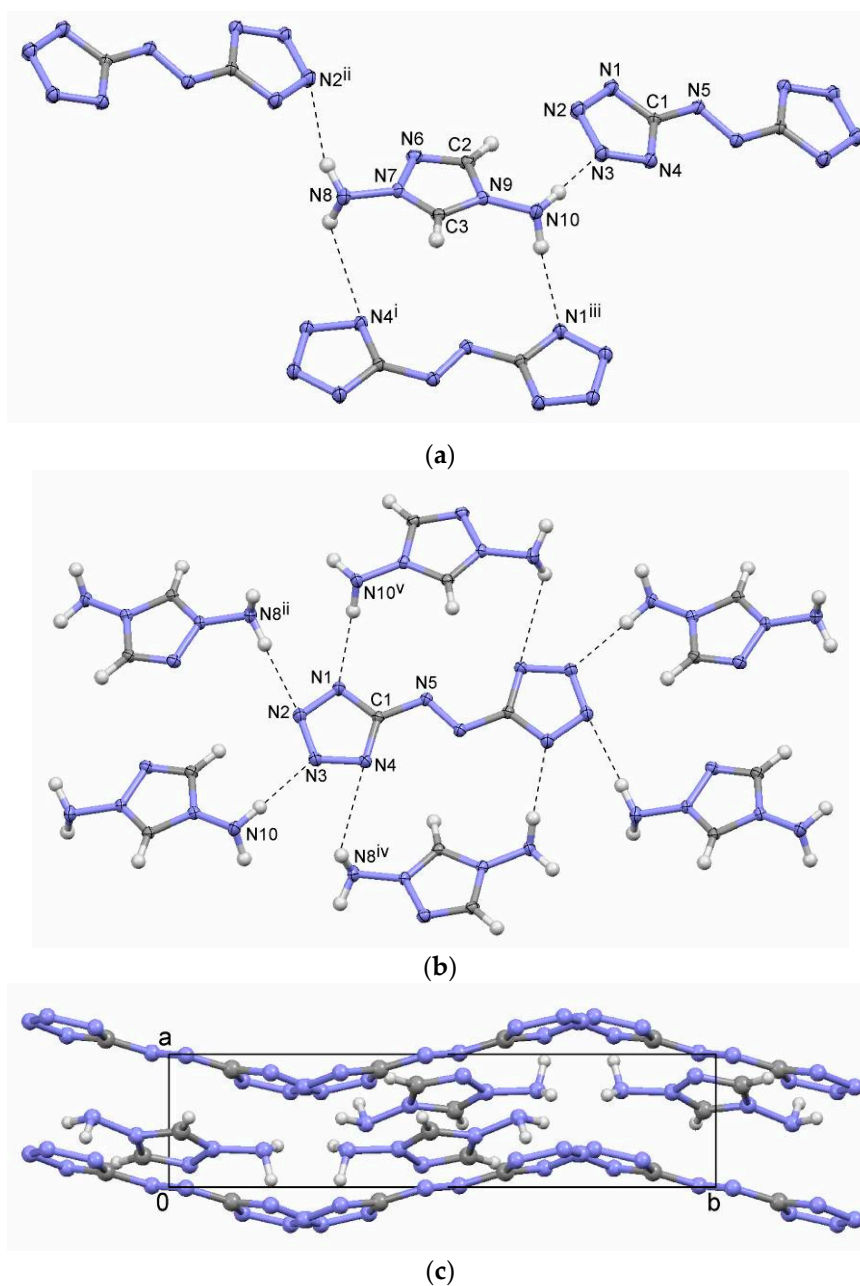


Figure 3. Bis(1,4-diamino-1,2,4-triazolium)5,5'-azotetrazolate (**2**). (a) The cation as hydrogen-bond donor; (b) The anion as hydrogen-bond acceptor; (c) Wave-like arrangement of the ions in the unit cell. Symmetry codes: (i) $-x, -1/2 + y, 1/2 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 3/2 - y, -1/2 + z$; (iv) $-x, 1/2 + y, 1/2 - z$; (v) $x, 3/2 - y, 1/2 + z$.

2.3. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Thermoanalysis of the triazolium salts **1** and **2** showed initial melting followed by exothermal decomposition (maxima at 164 and 165 °C) with approximately 60% loss of mass. Decomposition gases are not limited to N₂, but also include NH₃, CH₄ and HCN [6], which are formed in varying amounts. Thermograms are depicted in Figure 4.

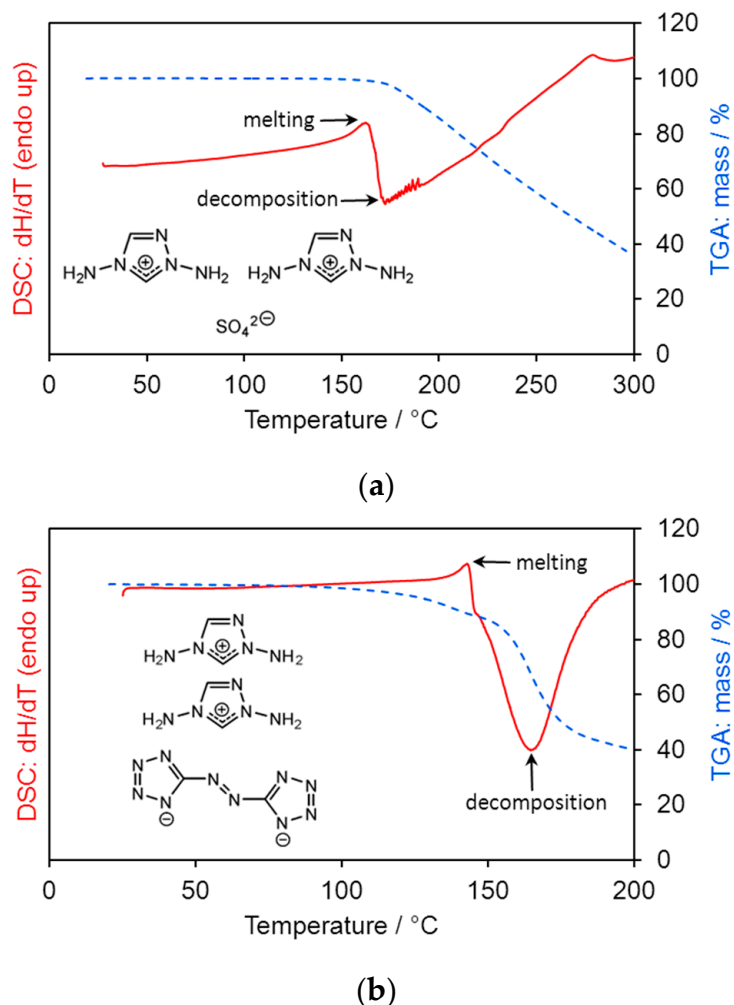


Figure 4. DSC and TGA of (a) bis(1,4-diamino-1,2,4-triazolium) sulfate (**1**) and (b) 5,5'-azotetrazolate (**2**). Heating rate 10 °C·min^{−1}.

3. Experimental Section

1,4-Diamino-1,2,4-triazolium chloride [CASRN 122583-43-1] was prepared as previously described [12]. Barium 5,5'-azotetrazolate pentahydrate [CASRN 441747-65-5] was prepared according to a published procedure [13]. All other chemicals were purchased from Sigma-Aldrich (Steinheim, Germany). NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer (Billerica, MA, USA). IR spectra were obtained with a Bruker Alpha FT (Billerica, MA, USA) instrument. DSC was performed with a DSC 7 (Perkin-Elmer, Norwalk, CT, USA) applying a heating rate of 10 °C·min^{−1}. TGA was carried out with a TGA 7 system (Perkin-Elmer) at a heating rate of 10 °C·min^{−1}.

Single crystal diffraction intensity data were recorded by ω scans with an Oxford Diffraction Gemini-R Ultra (Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK) or by φ and ω scans with a Bruker D8 Quest Photon 100 (Billerica, MA, USA) diffractometer using MoK α radiation. CCDC reference numbers: 1441522 and 1441523. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (Cambridge, UK).

3.1. Bis(1,4-diamino-1,2,4-triazolium) Sulfate (**1**)

A solution of 1,4-diamino-1,2,4-triazolium chloride (0.65 g, 4.8 mmol) in hot H₂O (30 mL) was added to a solution of Ag₂SO₄ (0.75 g, 2.4 mmol) in hot H₂O (60 mL). The mixture was sonicated for 10 minutes, and the precipitate was removed by centrifugation. The supernatant was taken to

dryness under reduced pressure, and the residue was crystallized from hot MeOH. Single crystals were obtained by slow diffusion of MeOH into a H₂O/2-PrOH solution. Yield: 0.64 g (90%). M.p. 151–154 °C (decomposition). ¹H NMR (DMSO-d₆, 300 MHz): δ 6.9 (br s, 2H), 7.4 (br s, 2H), 9.06 (s, 1H), 10.20 (s, 1H) ppm. IR (neat): $\tilde{\nu}$ 3216 (m), 3119 (m), 2991 (m), 1646 (w), 1409 (w), 1053 (s), 985 (m), 974 (m), 901 (m), 751 (w), 652 (w), 605 (s), 488 (m) cm^{−1}.

3.2. Bis(1,4-diamino-1,2,4-triazolium) 5,5'-Azotetrazolate (2)

A solution of bis(1,4-diamino-1,2,4-triazolium) sulfate (50 mg, 0.17 mmol) in H₂O (2 mL) was added to a suspension of barium 5,5'-azotetrazolate pentahydrate (66 mg, 0.17 mmol) in H₂O (4 mL). The mixture was stirred at 20 °C for 72 h, and the precipitate was removed by filtration through a 0.45 µm filter. The clear filtrate was taken to dryness at 20 °C under reduced pressure (0.1 mbar) to yield a yellow powder (60 mg, 98%). Single crystals were obtained by slow diffusion of Et₂O into a MeOH solution. M.p. 135 °C (decomposition). ¹H NMR (DMSO-d₆, 300 MHz): δ 7.05 (s, 2H), 7.46 (s, 2H), 9.10 (s, 1H), 10.28 (s, 1H) ppm. ¹³C NMR (DMSO-d₆, 75 MHz): δ 140.9, 143.5, 173.3 ppm. IR (neat): $\tilde{\nu}$ 3313 (w), 3213 (w), 3171 (w), 3085 (m), 2998 (m), 2919 (m), 1627 (m), 1442 (m), 1390 (s), 1171 (m), 1159 (m), 1081 (m), 1047 (m), 1019 (s), 953 (s), 897 (m), 732 (s), 650 (s), 625 (s), 608 (s) cm^{−1}.

4. Conclusions

One can still find small and simple molecules which are neglected in the literature—in other words, hidden treasures. The 1,4-diamino-1,2,4-triazolium cation is one of those. Intricate networks of hydrogen bonds are observed in the crystal structures of two nitrogen-rich salts.

Author Contributions: Gerhard Laus conceived and designed this study, carried out experimental work (synthesis, crystallization and characterization) and wrote the manuscript. Klaus Wurst and Volker Kahlenberg determined the crystal structures. Herwig Schottenberger contributed conceptual details and supported this study.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Link, H.; Klötzer, W.; Karpitschka, E.M.; Montavon, M.; Müssner, R.; Singewald, N. 1-Amino- and 1,3-Diaminoimidazolium Salts. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 556–557. [[CrossRef](#)]
- Laus, G.; Kahlenberg, V.; Többers, D.M.; Jetty, R.K.R.; Griesser, U.J.; Schütz, J.; Kristeva, E.; Wurst, K.; Schottenberger, H. Lattice architecture and hydrogen-bonding networks of *N*-aminoazolium and *N,N'*-diaminoazolium chlorides. *Cryst. Growth Des.* **2006**, *6*, 404–410. [[CrossRef](#)]
- Thiele, J. Ueber Azo- und Hydrazoverbindungen des Tetrazols. *Ann. Chem.* **1898**, *303*, 57–75. (In German). [[CrossRef](#)]
- Laus, G.; Kahlenberg, V.; Wurst, K.; Schottenberger, H.; Fischer, N.; Stierstorfer, J.; Klapötke, T.M. Synthesis and crystal structures of new 5,5'-azotetrazolates. *Crystals* **2012**, *2*, 127–136. [[CrossRef](#)]
- Lampl, M.; Laus, G.; Braun, D.E.; Kahlenberg, V.; Wurst, K.; Fuhrmann, G.; Schottenberger, H.; Huppertz, H. New crystal structures in the realm of 5,5'-azotetrazolates. *Z. Naturforsch.* **2015**, *70*, 125–134. [[CrossRef](#)]
- Klapötke, T.M.; Sabaté, C.M. New energetic compounds based on the nitrogen-rich 5,5'-azotetrazolate anion ([C₂N₁₀]^{2−}). *New J. Chem.* **2009**, *33*, 1605–1617. [[CrossRef](#)]
- Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J.M. Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5,5'-bis(tetrazolate). *Chem. Commun.* **2005**, *21*, 2750–2752. [[CrossRef](#)] [[PubMed](#)]
- Laus, G.; Wurst, K.; Schottenberger, H. Crystal structure of bis(1,3-diaminoimidazolium) 5,5'-azotetrazolate, (C₃H₇N₄)₂ (C₂N₁₀), C₈H₁₄N₁₈. *Z. Kristallogr. New Cryst. Struct.* **2012**, *227*, 293–294. [[CrossRef](#)]
- Laus, G.; Kahlenberg, V.; Schottenberger, H. Crystal structure of 1,3-diaminoimidazolium hexafluorophosphate, [C₃H₇N₄]⁺PF₆[−]. *Z. Kristallogr. New Cryst. Struct.* **2010**, *225*, 463–464. [[CrossRef](#)]
- Bentivoglio, G.; Schwärzler, A.; Wurst, K.; Kahlenberg, V.; Nauer, G.; Bonn, G.; Schottenberger, H.; Laus, G. Hydrogen Bonding in the Crystal Structures of New Imidazolium Triflimide Protic Ionic Liquids. *J. Chem. Cryst.* **2009**, *39*, 662–668. [[CrossRef](#)]

11. Bernstein, J.; Davis, R.E.; Shimoni, L.; Chang, N.-L. Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555–1573. [[CrossRef](#)]
12. Laus, G.; Klötzer, W. Synthesis of 1-amino-1H-1,2,4-triazoles. *Synthesis* **1989**, *4*, 269–272. [[CrossRef](#)]
13. Hammerl, A.; Holl, G.; Klapötke, T.M.; Mayer, P.; Nöth, H.; Piotrowski, H.; Warchhold, M. Salts of 5,5'-azotetrazolate. *Eur. J. Inorg. Chem.* **2002**, *4*, 834–845. [[CrossRef](#)]



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