

Article

Crystal Structures of New Ammonium 5-Aminotetrazolates

Martin Lampl ¹, Robert Salchner ¹, Gerhard Laus ¹, Doris E. Braun ², Volker Kahlenberg ³, Klaus Wurst ¹, Gerda Fuhrmann ¹, Herwig Schottenberger ¹ and Hubert Huppertz ^{1,*}

¹ Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, 6020 Innsbruck, Austria; E-Mails: martin.lampl@uibk.ac.at (M.L.); robert.salchner@uibk.ac.at (R.S.); gerhard.laus@uibk.ac.at (G.L.); klaus.wurst@uibk.ac.at (K.W.); gerda.fuhrmann@uibk.ac.at (G.F.); herwig.schottenberger@uibk.ac.at (H.S.)

² Institute of Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria;
E-Mail: doris.braun@uibk.ac.at

³ Institute of Mineralogy and Petrography, University of Innsbruck, 6020 Innsbruck, Austria;
E-Mail: volker.kahlenberg@uibk.ac.at

* Author to whom correspondence should be addressed; E-Mail: hubert.huppertz@uibk.ac.at;
Tel.: +43-512-507-57000; Fax: +43-512-507-57099.

External Editor: Nikolaus Korber

Received: 16 September 2014; in revised form: 30 October 2014 / Accepted: 13 November 2014 /

Published: 19 November 2014

Abstract: The crystal structures of three salts of anionic 5-aminotetrazole are described. The tetramethylammonium salt ($P\bar{1}$) forms hydrogen-bonded ribbons of anions which accept weak C–H···N contacts from the cations. The cystamine salt ($C2/c$) shows wave-shaped ribbons of anions linked by hydrogen bonds to screw-shaped dicationic layers. The tetramethylguanidine salt ($P2_1/c$) exhibits layers of anions hydrogen-bonded to the cations.

Keywords: 5-aminotetrazole; cystamine; tetramethylammonium; tetramethylguanidine

1. Introduction

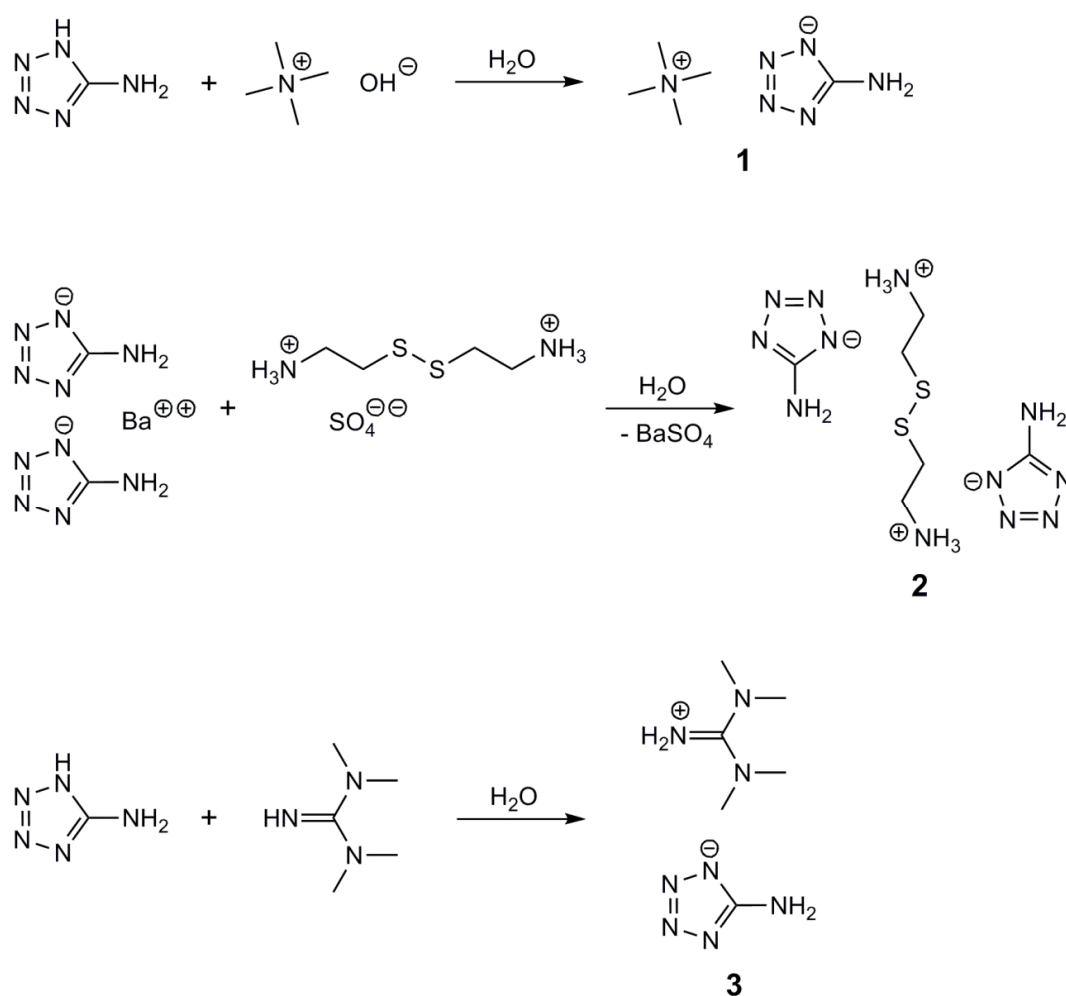
Due to its amphiprotic nature [1,2], 5-aminotetrazole has served as a cation [3,4] or as an anion in energetic salts [5]. Crystal structures of several alkali metal 5-aminotetrazolates have been reported [6]. Organic salts containing 5-aminotetrazole as anion have been first described more than six decades ago [7]. Continuing our interest in nitrogen-rich heterocycles [8–11], we describe here the preparation

and crystal structures of three new 5-aminotetrazolates of organic cations. These salts are of interest as blowing agents [12] and as alternative precursors for nitridosilicates [13–15]. Following the structural characterization, the new compounds were examined by DSC and TGA in order to assess their suitability for those purposes.

2. Results and Discussion

Three synthetic methods were employed to generate the required 5-aminotetrazolate anion (Figure 1), *i.e.*, (a) deprotonation of 5-aminotetrazole by an organic hydroxide; (b) ion metathesis of an organic sulfate with barium 5-aminotetrazolate; and (c) direct reaction of 5-aminotetrazole with a strong organic base.

Figure 1. Synthesis of the 5-aminotetrazolates 1–3.



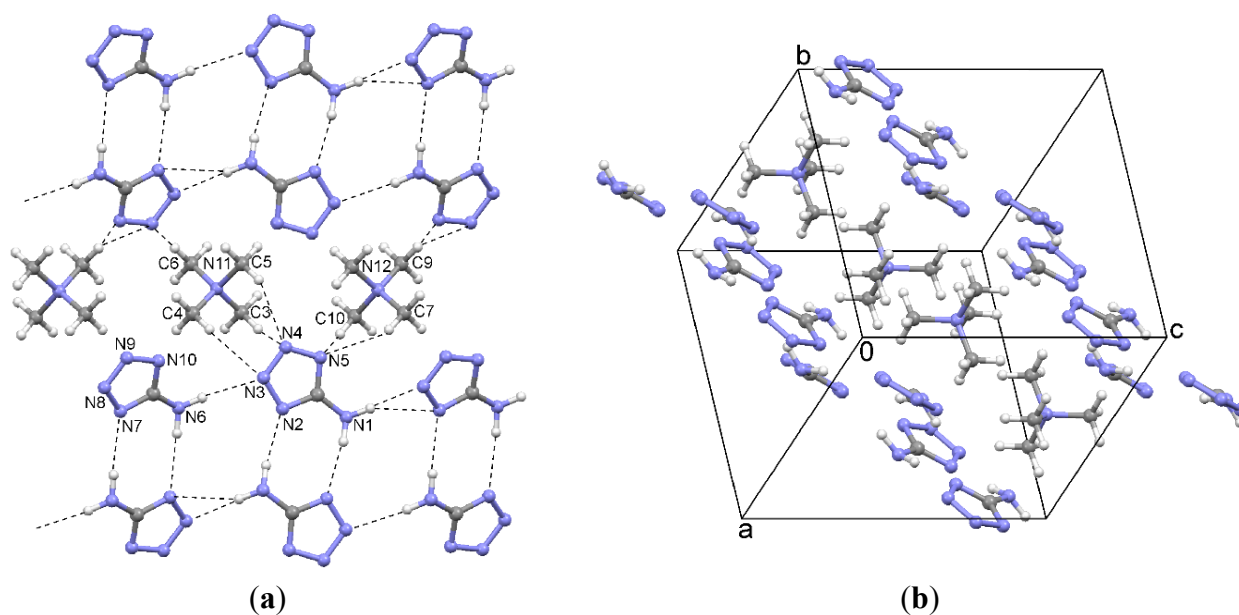
The crystal data and details of the structure refinements for tetramethylammonium 5-aminotetrazolate (**1**); cystamine bis(5-aminotetrazolate) (**2**); and 1,1,3,3-tetramethylguanidinium 5-aminotetrazolate (**3**) are summarized in Table 1.

Table 1. Crystal data and structure refinement details for compounds 1–3.

Compound	1	2	3
CCDC No.	1024084	1024085	1024086
Chemical formula	C ₄ H ₁₂ N·CH ₂ N ₅	C ₄ H ₁₄ N ₂ S ₂ ·2(CH ₂ N ₅)	C ₅ H ₁₄ N ₃ ·CH ₂ N ₅
<i>M_r</i> /g·mol ^{−1}	158.22	322.44	200.27
Crystal size/mm ³	0.24 × 0.16 × 0.10	0.30 × 0.30 × 0.20	0.40 × 0.40 × 0.40
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.1270(9)	17.4437(3)	7.5109(4)
<i>b</i> /Å	10.129(1)	7.9305(3)	12.4241(4)
<i>c</i> /Å	10.432(2)	11.1625(4)	11.6513(4)
α /°	98.86(1)	—	—
β /°	110.65(2)	110.13(1)	106.82(1)
γ /°	106.77(1)	—	—
<i>V</i> /Å ³	828.2(2)	1449.85(8)	1040.72(7)
<i>Z</i>	4	4	4
<i>D_x</i> /g·cm ^{−3}	1.27	1.48	1.28
η	0.09	0.38	0.09
<i>F</i> (000)/e	344	680	432
Temperature/K	173(2)	233(2)	173(2)
$\theta_{\max}$ /°	25.4	26.0	28.6
<i>h</i> , <i>k</i> , <i>l</i> range	−10 ≤ <i>h</i> ≤ 9 −12 ≤ <i>k</i> ≤ 12 −12 ≤ <i>l</i> ≤ 11	−21 ≤ <i>h</i> ≤ 21 −9 ≤ <i>k</i> ≤ 9 −13 ≤ <i>l</i> ≤ 13	−9 ≤ <i>h</i> ≤ 8 −14 ≤ <i>k</i> ≤ 14 −14 ≤ <i>l</i> ≤ 12
Absorption correction	multi-scan	—	multi-scan
Measured reflections	5042	4661	6125
Independent reflections (<i>R</i> _{int})	3010 (0.030)	1418 (0.026)	1897 (0.021)
Observed reflections (<i>I</i> ≥ 2σ(<i>I</i>))	2317	1285	1718
Restraints/parameters	0/224	5/112	0/148
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> ≥ 2σ(<i>I</i>))	0.042, 0.091	0.031, 0.081	0.033, 0.083
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.062, 0.106	0.034, 0.083	0.038, 0.087
Goodness of fit	1.02	1.12	1.06
Δρ _{max} , Δρ _{min} /e Å ^{−3}	0.21, −0.19	0.21, −0.38	0.36, −0.16

2.1. Tetramethylammonium 5-Aminotetrazolate (1)

Two independent ion pairs are observed in the asymmetric unit. The tetrazolate anions arranged in ribbons parallel to the ($\bar{1}$ 11) plane accept weak C–H···N contacts from the quaternary cations which are aligned in rows parallel to the $[1 \bar{1} 1]$ direction (Figure 2a). The rows of cations are located sideways between the ribbons and above/below the plane of the ribbons, as displayed in Figure 2b. The hydrogen bond parameters are collected in Table 2. Phase purity of the bulk sample was confirmed by Pawley fit between the experimental and the calculated powder patterns (Figure 3 and Table 3).

Figure 2. (a) Interactions in the crystal structure of **1**; (b) Packing diagram of **1**.**Table 2.** Hydrogen bond parameters (Å, °).

Compound	Interaction	H...A	D...A	D-H...A	Symmetry Operation A
1	N1-H12...N2	2.17(3)	3.043(3)	170(2)	$2 - x, 1 - y, 1 - z$
	N6-H61...N3	2.25(2)	3.143(2)	173(2)	x, y, z
	N6-H62...N7	2.25(2)	3.150(2)	177(2)	$1 - x, 1 - y, -z$
	N1-H11...N7	2.51(2)	3.385(2)	159(2)	$1 + x, y, 1 + z$
	N1-H11...N8	2.61(2)	3.462(3)	155(2)	$1 + x, y, 1 + z$
	C9-H...N9	2.562	3.511(3)	162.9	$1 - x, -y, 1 - z$
	C4-H...N3	2.591	3.520(2)	158.3	x, y, z
	C5-H...N4	2.592	3.474(2)	149.7	x, y, z
	C3-H...N4	2.601	3.480(3)	149.3	x, y, z
	C10-H...N5	2.616	3.497(3)	149.6	x, y, z
	C9-H...N10	2.644	3.542(3)	152.5	$1 - x, -y, 1 - z$
	C7-H...N5	2.652	3.524(3)	148.3	x, y, z
	C6-H...N9	2.652	3.551(2)	152.7	$-x, -y, -z$
2	N6-H...N4	1.98(2)	2.870(2)	175(2)	$x, -y, -1/2 + z$
	N6-H...N3	2.05(1)	2.893(2)	162(2)	x, y, z
	N6-H...N5	2.07(1)	2.958(2)	164(1)	$1/2 - x, -1/2 + y, 5/2 - z$
	N5-H...N2	2.16(2)	3.037(2)	174(2)	$x, -y, 1/2 + z$
	N5-H...N1	2.20(2)	3.070(2)	173(2)	$1 - x, -y, 3 - z$
3	N8-H...N2	2.04(2)	2.921(2)	169(1)	$1 - x, -y, 1 - z$
	N8-H...N4	2.05(2)	2.937(1)	166(1)	$1 - x, -1/2 + y, 3/2 - z$
	N1-H...N5	2.21(2)	3.080(2)	169(1)	$1 - x, 1 - y, 1 - z$

Figure 3. Pawley fit ($R_{wp} = 12.11\%$, $R_{exp} = 5.47\%$, $R_p = 8.66\%$, $gof = 2.21$) of the powder X-ray diffraction (PXRD) data of **1** with a model calculated from the structure parameters derived from the single crystal structure. Black dots indicate raw data, while the red line indicates the calculated model. Tick marks (blue) are the 2θ positions for the hkl reflections. The difference curve is shown in green.

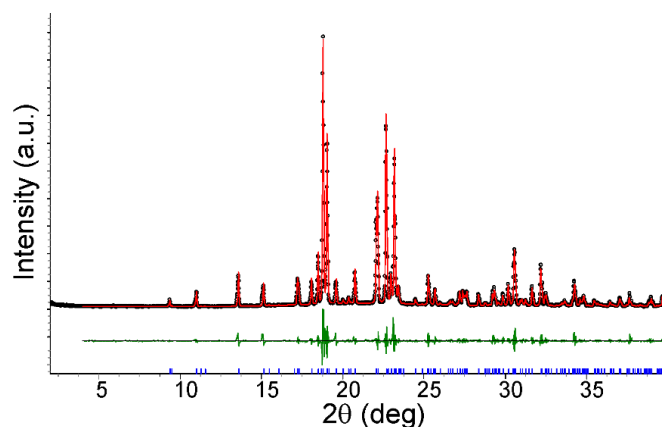


Table 3. Comparison of lattice parameters determined at 173 K (single crystal X-ray diffraction data, SCXRD) and 298 K (powder X-ray diffraction data).

1	SG	$D_x/\text{g}\cdot\text{cm}^{-3}$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
SCXRD	$P\bar{1}$	1.27	9.1270(9)	10.129(2)	10.432(2)	98.86(1)	110.65(2)	106.77(1)
PXRD	$P\bar{1}$	1.24	9.2743(5)	10.1495(5)	10.5227(6)	98.72(1)	110.81(1)	106.91(1)

2.2. Cystamine Bis(5-aminotetrazolate) (**2**)

The fragments of the cystamine cations are completed by a two-fold rotation axis perpendicular to the S1–S1 bond. The resulting dication is screw-shaped with a C–S–S–C dihedral angle of $89.6(1)^\circ$ (Figure 4a). The anions form hydrogen-bonded wave-shaped ribbons parallel to the ac plane to which the cations are linked by hydrogen bonds (Figure 4b). The Pawley fit is depicted in Figure 5, and the corresponding results are shown in Table 4.

Figure 4. (a) Interactions in the crystal structure of **2**; $i: -x, y, 3/2 - z$; (b) Packing diagram.

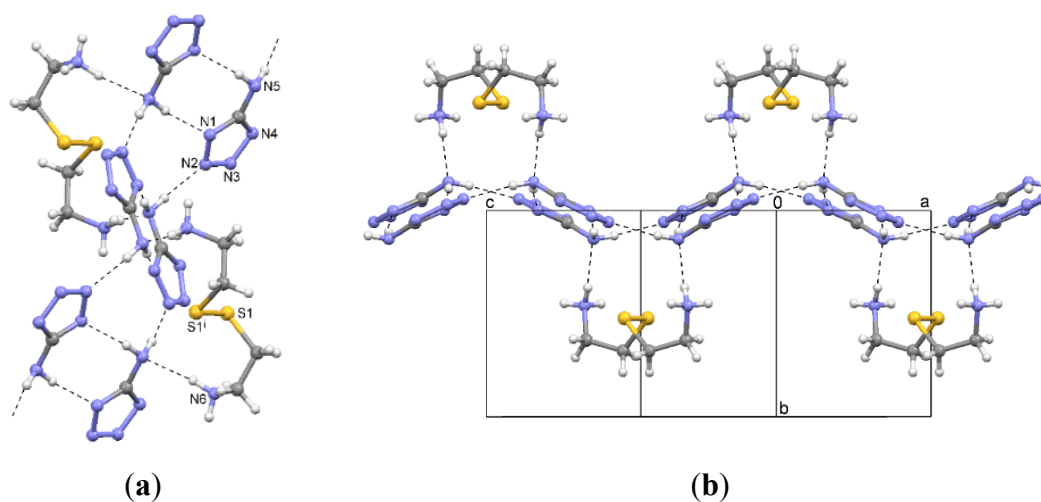


Figure 5. Pawley fit ($R_{wp} = 9.04\%$, $R_{exp} = 7.96\%$, $R_p = 6.89\%$, $gof = 1.14$) of the PXRD data of **2** with a model calculated from the structural data of the single crystal structure determination.

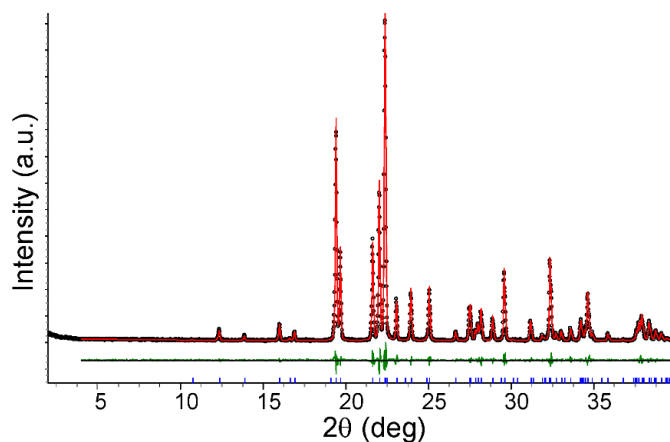


Table 4. Comparison of lattice parameters determined at 233 K (single crystal X-ray diffraction data) and 298 K (powder X-ray diffraction data).

2	$D_x/\text{g}\cdot\text{cm}^{-3}$	Space Group	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$
SCXRD	1.48	$C2/c$	17.4437(3)	7.9305(3)	11.1625(4)	110.131(2)
PXRD	1.47	$C2/c$	17.4964(6)	7.9400(3)	11.1614(4)	110.253(3)

2.3. 1,1,3,3-Tetramethylguanidinium 5-Aminotetrazolate (**3**)

The crystal structure of **3** is composed of hydrogen-bonded layers of anions and cations (Figure 6a) arranged parallel to the bc plane (Figure 6b). The Pawley fit is shown in Figure 7, and the corresponding results are collected in Table 5.

Figure 6. (a) Interactions in the crystal structure of **3**; (b) Packing diagram of **3**; hydrogen atoms are omitted for clarity.

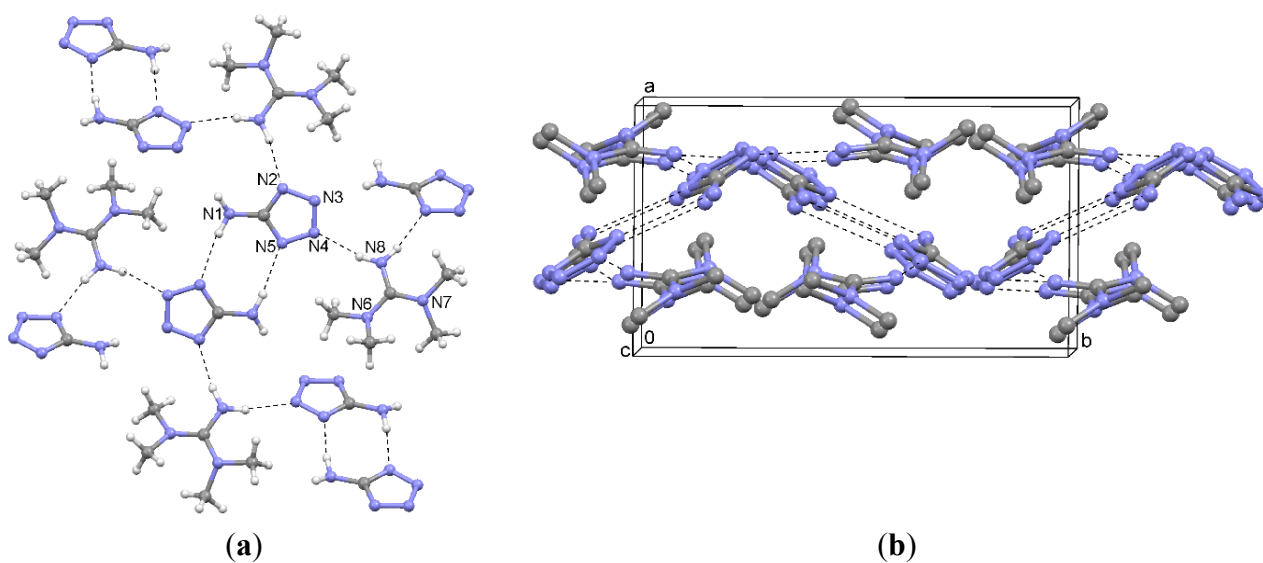


Figure 7. Pawley fit ($R_{wp} = 10.03\%$, $R_{exp} = 5.57\%$, $R_p = 7.80\%$, $gof = 1.80$) of the PXRD data of **3** with a model calculated from the structural data of the single crystal structure determination.

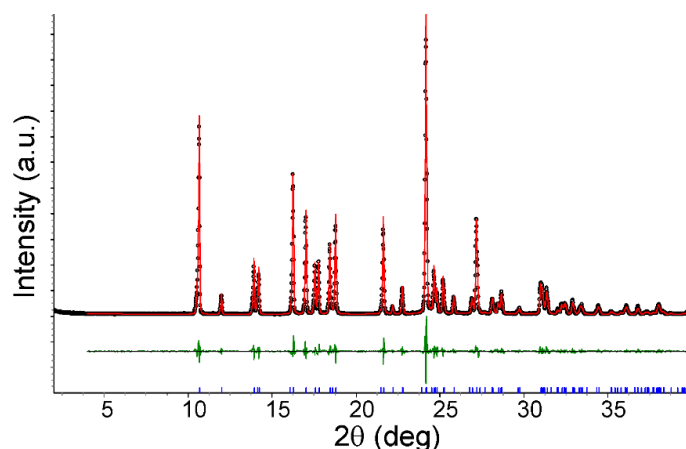


Table 5. Comparison of lattice parameters determined at 173 K (single crystal X-ray diffraction data) and 298 K (powder X-ray diffraction data).

3	$D_x/\text{g}\cdot\text{cm}^{-3}$	Space Group	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$
SCXRD	1.28	$P2_1/c$	7.5109(4)	12.4241(4)	11.6513(4)	106.82(1)
PXRD	1.25	$P2_1/c$	7.6944(2)	12.5188(5)	11.5183(6)	107.03(1)

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

Thermoanalysis of the 5-aminotetrazolates **1–3** showed an extensive decomposition with loss of mass around the melting temperature. The pertinent thermograms are depicted in Figure 8. Since the decomposition is not exothermic, the new compounds are not “energetic salts” in a strict sense, but appear to be suitable as temperate blowing agents.

Figure 8. Differential Scanning Calorimetry/Thermogravimetric Analysis (DSC/TGA) thermograms of (a) **1**; (b) **2**; and (c) **3**.

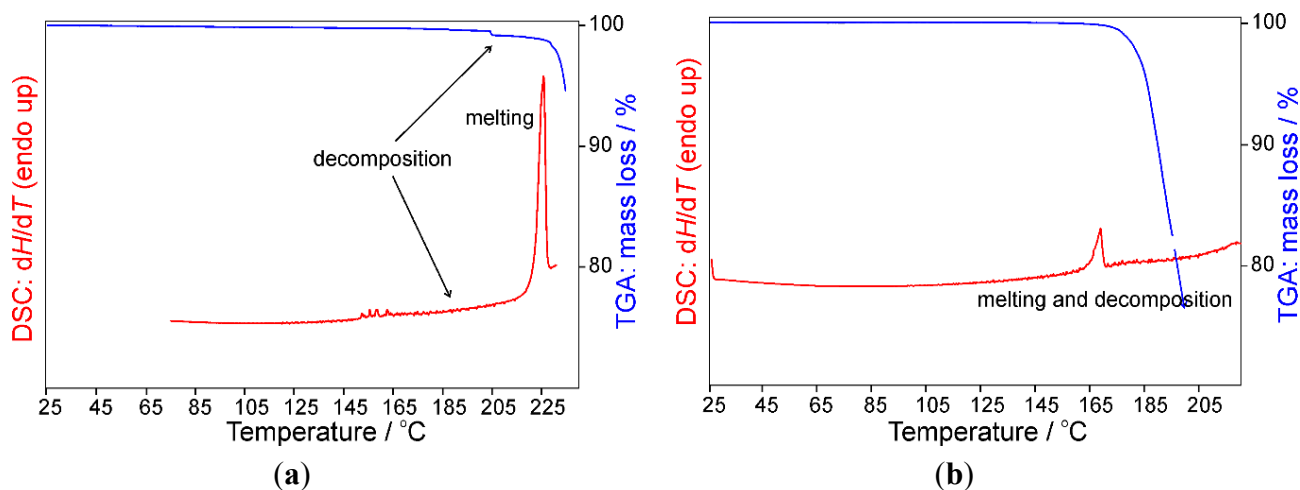
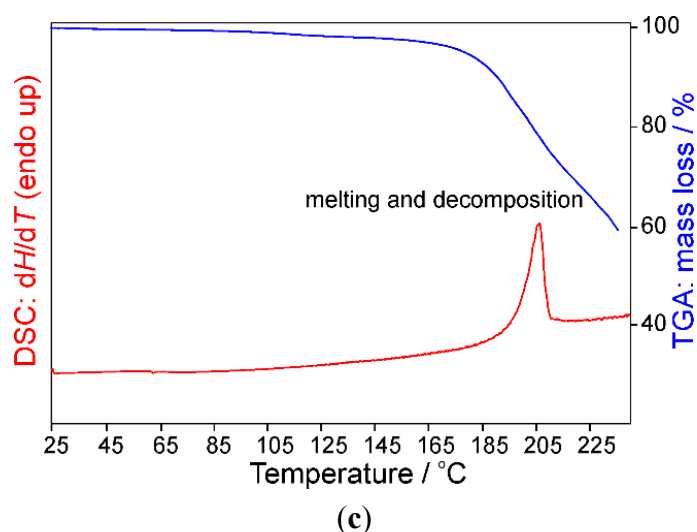


Figure 8. Cont.



3. Experimental Section

Barium 5-aminotetrazolate tetrahydrate was prepared according to a published procedure [16]. All other chemicals were purchased from Sigma-Aldrich, St. Louis, MO, USA (European affiliate, Steinheim, Germany). NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer (Billerica, MA, USA). IR spectra were obtained with an Alpha FT (Bruker) instrument. Elemental analyses were conducted at the University of Vienna, Austria. DSC was performed with a DSC 7 (Perkin-Elmer, Norwalk, CT, USA) applying a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. TGA was carried out with a TGA 7 system (Perkin-Elmer) at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. XRPD patterns were obtained using a X'Pert PRO diffractometer (PANalytical, Almelo, The Netherlands) equipped with a theta/theta coupled goniometer in transmission geometry, programmable XYZ stage with well plate holder, $\text{CuK}\alpha_{1,2}$ radiation source with a focussing mirror, a 0.5° divergence slit and a 0.02° Soller slit collimator on the incident beam side, a 2 mm antiscattering slit and a 0.02° Soller slit collimator on the diffracted beam side and a 255 channel solid state PIXcel detector. The patterns were recorded, unless stated otherwise, at a tube voltage of 40 kV, tube current of 40 mA, applying a step size of $2\theta = 0.013^{\circ}$ with 400 s per step in the 2θ range between 2° and 40° . Pawley fits were performed with Topas Academic V5 (Coelho Software, Brisbane, Australia). The background was modelled with Chebyshev polynomials and the modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) function was used for peak shape fitting. Single crystal diffraction intensity data were recorded by ω scans with an Oxford Diffraction Gemini-R Ultra (Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK) diffractometer (for **1** and **3**) or by ϕ and ω scans with a Nonius KappaCCD (Bruker, Billerica, MA, USA) diffractometer (for **2**) using $\text{MoK}\alpha$ radiation. CCDC reference numbers: 1024084–1024086. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (Cambridge, UK).

3.1. Tetramethylammonium 5-Aminotetrazolate (**1**)

5-Aminotetrazole monohydrate (866 mg, 8.40 mmol) was added to a solution of tetramethyl-ammonium hydroxide pentahydrate (1.52 g, 8.40 mmol) in H_2O (10 mL). The mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 20 min to give a clear solution. The solvent was removed under reduced pressure, and the residue was

recrystallized from hot MeOH. Yield: 1.11 g (84%). M.p. 223–225 °C (decomposition). ^1H -NMR (DMSO- d_6 , 300 MHz): δ 3.10 (s, 12H, CH_3), 3.9 (br s, 2H, NH_2) ppm. ^{13}C -NMR (DMSO- d_6 , 75 MHz): δ 54.3 (4C, CH_3), 164.1 (tetrazole) ppm. IR (neat): $\tilde{\nu}$ 3346 m, 3144 w, 3030 w, 1508 s, 1486 s (ν C = N), 1447 m, 1198 w, 1118 m, 949 s, 892 m, 750 $\text{m}\cdot\text{cm}^{-1}$. $\text{C}_5\text{H}_{14}\text{N}_6$ (158.20): calculated C 37.96, H 8.92, N 53.12; found C 37.67, H 9.17, N 52.97.

3.2. Cystamine Bis(5-Aminotetrazolate) (2)

Cystamine sulfate monohydrate (320 mg, 1.19 mmol) was added to a solution of barium 5-aminotetrazolate tetrahydrate (450 mg, 1.19 mmol) in H_2O (10 mL). The mixture was stirred for 15 min, and the precipitate was removed by filtration. The filtrate was taken to dryness under reduced pressure, and the residue was recrystallized from hot $\text{H}_2\text{O}/\text{EtOH}$ (1:4) to yield 320 mg (83%) of the colorless product. These crystals were suitable for structure determination. M.p. 165–167 °C (decomposition). ^1H -NMR (DMSO- d_6 , 300 MHz): δ 2.77–2.81 and 2.88–2.93 (AA'BB', 8H, CH_2CH_2), 6.3 (br, 10H, NH_2 and NH_3) ppm. ^{13}C NMR (DMSO- d_6 , 75 MHz): δ 39.4 (CH_2), 39.9 (CH_2), 159.0 (tetrazole) ppm. IR (neat): $\tilde{\nu}$ 3226 w, 3127 w, 2911 w, 2852 w, 2635 w, 2542 w, 2493 w, 1538 m, 1511 s (ν C=N), 1450 m, 1404 m, 1215 w, 1136 m, 1118 m, 900 s, 813 m, 442 $\text{s}\cdot\text{cm}^{-1}$. $\text{C}_6\text{H}_{18}\text{N}_{12}\text{S}_2$ (322.42): calculated C 22.35, H 5.63, N 52.13, S 19.89; found C 22.52, H 5.63, N 52.23, S 19.82.

3.3. 1,1,3,3-Tetramethylguanidinium 5-Aminotetrazolate (3)

1,1,3,3-Tetramethylguanidine (1.4 mL, 11.2 mmol) was added to a stirred suspension of 5-aminotetrazole monohydrate (1.0 g, 9.7 mmol) in H_2O (10 mL) to give a clear solution. The solvent was removed under reduced pressure, and the residue was vacuum-dried for 3 h to yield 1.90 g (98%) of the colorless product. Single crystals were obtained by slow evaporation of a solution in MeOH. M.p. 200 °C (decomposition). ^1H NMR (DMSO- d_6 , 300 MHz): δ 2.88 (s, 12H, CH_3) ppm. ^{13}C -NMR (DMSO- d_6 , 75 MHz): δ 40.0 (4C, CH_3), 161.4 (C= NH_2), 163.8 (tetrazole) ppm. IR (neat): $\tilde{\nu}$ 3409 w, 3180 w, 2904 m, 1600 s, 1573 s, 1518 s (ν C=N), 1438 m, 1414 s, 1096 m, 1066 m, 1036 m, 998 w, 768 w, 708 m, 436 $\text{m}\cdot\text{cm}^{-1}$. $\text{C}_6\text{H}_{16}\text{N}_8$ (200.24): calculated C 35.99, H 8.05, N 55.96; found C 36.19, H 8.26, N 55.24.

4. Conclusions

Three new ammonium 5-aminotetrazolates were prepared, and their crystal structures were determined. They appear to be promising candidates as gas-releasing agents, as indicated by thermal analysis.

Acknowledgments

We gratefully acknowledge funding by Die Österreichische Forschungsförderungsgesellschaft (FFG, Project 841104). Doris E. Braun gratefully acknowledges funding by the Hertha Firnberg Program of the Austrian Science Fund (FWF, Project T593-N19).

Author Contributions

Martin Lampl and Robert Salchner carried out experimental work (synthesis, crystallization and characterization). Gerhard Laus prepared the manuscript. Doris E. Braun contributed powder patterns and thermoanalyses. Volker Kahlenberg and Klaus Wurst determined the crystal structures. Gerda Fuhrmann contributed spectroscopic measurements. Herwig Schottenberger and Hubert Huppertz conceived and designed the study.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Boraei, A.A.A. Acidity constants of some tetrazole compounds in various aqueous-organic solvent media. *J. Chem. Eng. Data* **2001**, *46*, 939–943.
2. Albert, A.; Goldacre, R.; Phillips, J. The strength of heterocyclic bases. *J. Chem. Soc.* **1948**, *2*, 2240–2249.
3. Von Denffer, M.; Klapötke, T.M.; Kramer, G.; Spiess, G.; Welch, J.M.; Heeb, G. Improved synthesis and X-ray structure of 5-aminotetrazolium nitrate. *Propellants Explos. Pyrotech.* **2005**, *30*, 191–195.
4. Klapötke, T.M.; Sabaté, C.M.; Stierstorfer, J. Hydrogen-bonding stabilization in energetic perchlorate salts: 5-Amino-1*H*-Tetrazolium perchlorate and its adduct with 5-amino-1*H*-tetrazole. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1867–1874.
5. Tao, G.-H.; Guo, Y.; Joo, Y.-H.; Twamley, B.; Shreeve, J.M. Energetic nitrogen-rich salts and ionic liquids: 5-Aminotetrazole (AT) as a weak acid. *J. Mater. Chem.* **2008**, *18*, 5524–5530.
6. Ernst, V.; Klapötke, T.M.; Stierstorfer, J. Alkali salts of 5-aminotetrazole—Structures and properties. *Z. Anorg. Allg. Chem.* **2007**, *633*, 879–887.
7. Henry, R.A. Salts of 5-aminotetrazole. *J. Am. Chem. Soc.* **1952**, *74*, 6303.
8. Laus, G.; Kahlenberg, V.; Wurst, K.; Hummel, M.; Schottenberger, H. 1,4-Diazabicyclo[2.2.2]-octane (DABCO) 5-aminotetrazolates. *Crystals* **2012**, *2*, 96–104.
9. 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.
10. Laus, G.; Wurst, K.; Schottenberger, H. Crystal structure of bis(1,3-diaminoimidazolium) 5,5'-azotetrazolate, (C₃H₇N₄)₂·(C₂N₁₀). *Z. Kristallogr. NCS* **2012**, *227*, 293–294.
11. Fischer, N.; Hüll, K.; Klapötke, T.M.; Stierstorfer, J.; Laus, G.; Hummel, M.; Froschauer, C.; Wurst, K.; Schottenberger, H. 5,5'-Azoxytetrazolates—A new nitrogen-rich dianion and its comparison to 5,5'-azotetrazolate. *Dalton Trans.* **2012**, *41*, 11201–11211.
12. Nakagawa, S.; Ogawa, H.; Tanaka, H.; Onishi, A. Blowing Agents of Tetrazoles and Their Derivatives. U.S. Patent US 5,646,292, 8 July 1997.
13. Zeuner, M.; Pagano, S.; Schnick, W. Nitridosilicates and oxonitridosilicates: From ceramic materials to structural and functional diversity. *Angew. Chem. Int. Ed.* **2011**, *50*, 7754–7775.
14. Schnick, W.; Huppertz, H. Nitridosilicates—A significant extension of silicate chemistry. *Chem. Eur. J.* **1997**, *3*, 679–683.

15. Schnick, W.; Schlieper, T.; Huppertz, H.; Köllisch, K.; Orth, M.; Bettenhausen, R.; Schwarze, B.; Lauterbach, R. Nitridosilicates—A significant extension of silicate chemistry. *Phosphorus Sulfur Silicon Relat. Elem.* **1997**, *124–125*, 163–172.
16. Damavarapu, R.; Klapötke, T.M.; Stierstorfer, J.; Tarantik, K.R. Barium salts of tetrazole derivatives—Synthesis and characterization. *Propellants Explos. Pyrotech.* **2010**, *35*, 395–406.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).