

Article

Synthesis and Crystal Structures of New 5,5'-Azotetrazolates

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Abstract: Five new 5,5'-azotetrazolate salts (amminsilver, trimethylsulfonium, tetramethyl-phosphonium, trimethylsulfoxonium, 2-(hydroxyethyl)trimethylammonium) were prepared and characterized. The crystal structures were determined by X-ray diffraction. Interactions between the ions are identified and discussed. The sensitivities of the highly energetic silver salt were measured by BAM (Bundesanstalt für Materialforschung und-prüfung) methods.

Keywords: azotetrazolate; cholin; phosphonium; silver; sulfonium; sulfoxonium

1. Introduction

Nitrogen-rich “energetic salts” have received considerable attention as propellants or gas generators [1,2]. These salts typically contain cations such as hydrazinium [3–5], ammonium and guanidinium [6], triazolium [7–10], tetrazolium [11,12], or tetraaminopiperazinium [13], sometimes involving additional azido groups [6,10]. Preferred anions are—beside azide, nitrate, perchlorate and picrate—dinitramide [7], nitroazolates [7,10,14,15], dianions such as 5,5'-bis(tetrazolate) [16] and, in

particular, 5,5'-azotetrazolate [3–6,11,12,16]. The synthesis of 5,5'-azotetrazolates was first reported by Thiele [17]. Beyond the much acclaimed use as explosives, nitrogen-rich heterocycles are also of interest as ligands in coordination chemistry. With respect to their performance as potential explosives or propellants powerful materials are obtained when nitrogen-rich cations (e.g., hydrazinium, guanidinium) are used. When ions with lower nitrogen and higher carbon content are employed, the resulting less energetic materials are still relevant. Due to their electrochemical or optical properties, technical applications such as molecular electronics are envisioned [18]. They also have potential as precursors of functional materials, for example in the synthesis of low-density, nanoporous metal foams [19].

Numerous crystal structures of 5,5'-azotetrazolate salts [3–8,11–13,16,20,21] have been reported, including a series of metal salts; specifically, alkali and alkaline earth metals [22,23], lanthanoids [24–26], Pb [27], Tl [28], Mn [29], Fe [30], Cu and Cd [31] form crystalline salts.

In the present work 5,5'-azotetrazolate salts comprising cations based on sulfur or phosphorus are reported. A not yet described salt of choline and a new energetic silver complex are also disclosed, the latter one showing high sensitivities belonging to the class of primary explosives.

2. Results and Discussion

The silver complex was prepared by slow diffusion of the components. The incorporated ammonia molecule has a phlegmatizing effect causing the product to be less sensitive than the pure silver salt. The other salts were synthesized by two metathetical steps (the $\text{Ag}_2\text{SO}_4/\text{Ba}$ azotetrazolate method) starting from the respective halogenides. Satisfactory crystals could be obtained with little effort by slow evaporation of solutions in water or methanol. The structures reported herein are centrosymmetric. In all cases the asymmetric unit contained one half of the planar azotetrazolate ion which is completed by inversion. The crystallographic data and structure refinement parameters of all structures 1–5 are gathered in Table 1.

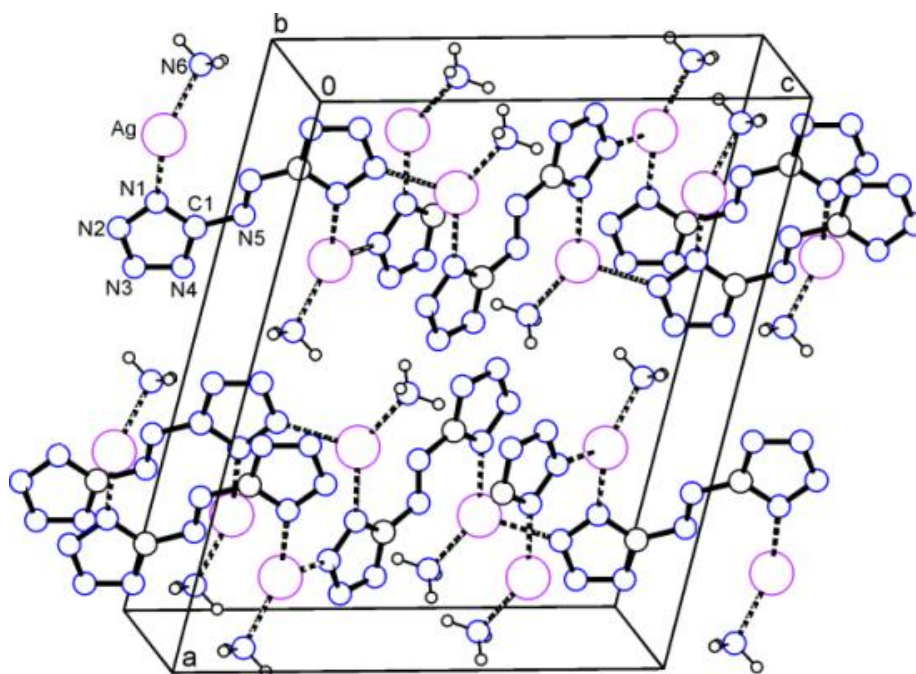
Table 1. Crystal data and structure refinement details for compounds 1–5.

Compound	1	2	3	4	5
CCDC no.	846911	846912	846913	846914	846915
Chemical formula	Ag ₂ (NH ₃) ₂ (C ₂ N ₁₀)	(C ₃ H ₉ S) ₂ (C ₂ N ₁₀)	(C ₄ H ₁₂ P) ₂ (C ₂ N ₁₀)	(C ₃ H ₉ OS) ₂ (C ₂ N ₁₀)	(C ₅ H ₁₄ NO) ₂ (C ₂ N ₁₀)
<i>M_r</i>	413.89	318.43	346.31	350.42	372.43
Crystal shape, color	plate, orange	prism, yellow	plate, orange	fragment, yellow	fragment, yellow
Crystal size/mm ³	0.1 × 0.1 × 0.06	0.44 × 0.36 × 0.24	0.36 × 0.32 × 0.12	0.2 × 0.2 × 0.2	0.40 × 0.24 × 0.24
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	18.0338(7)	5.9032(7)	5.9035(9)	5.2452(2)	5.4900(4)
<i>b</i> /Å	3.601(2)	7.4591(8)	13.388(2)	14.0290(4)	8.4206(6)
<i>c</i> /Å	14.906(3)	9.2538(8)	11.3173(19)	10.7735(4)	10.3003(6)
<i>α</i> /°	90	113.598(9)	90	90	78.564(5)
<i>β</i> /°	91.94(1)	98.370(8)	93.941(17)	102.036(3)	85.796(6)
<i>γ</i> /°	90	99.017(9)	90	90	81.876(6)
<i>V</i> /Å ³	967.4(6)	358.88(7)	892.4 (2)	775.34 (5)	461.53(6)
<i>Z</i>	8	2	4	4	2
<i>D_x</i> /g cm ^{−3}	2.84	1.47	1.29	1.50	1.34
<i>μ</i> /mm ^{−1}	4.04	0.38	0.26	0.37	0.10
<i>F</i> (000)/e	784	168	368	368	200
Diffractometer	Nonius KappaCCD	Gemini Ultra	Gemini-R Ultra	Gemini-R Ultra	Gemini-R Ultra
Data collection method	<i>φ</i> and <i>ω</i> scans	<i>ω</i> scans	<i>ω</i> scans	<i>Ω</i> scans	<i>ω</i> scans
Temperature/K	233	173	173	173	173
<i>θ</i> _{max} /°	24	25.4	25	28	25
<i>h</i> , <i>k</i> , <i>l</i> range	−19 ≤ <i>h</i> ≤ 20 −4 ≤ <i>k</i> ≤ 3 −16 ≤ <i>l</i> ≤ 17	−6 ≤ <i>h</i> ≤ 7 −8 ≤ <i>k</i> ≤ 5 −10 ≤ <i>l</i> ≤ 11	−5 ≤ <i>h</i> ≤ 7 −14 ≤ <i>k</i> ≤ 16 −15 ≤ <i>l</i> ≤ 13	−6 ≤ <i>h</i> ≤ 6 −18 ≤ <i>k</i> ≤ 17 −13 ≤ <i>l</i> ≤ 13	−6 ≤ <i>h</i> ≤ 5 −10 ≤ <i>k</i> ≤ 10 −12 ≤ <i>l</i> ≤ 10
Absorption correction	none	multi-scan	multi-scan	multi-scan	none
Measured reflections	1927	2168	3626	6332	3070
Independent reflections (<i>R</i> _{int})	739 (0.028)	1288 (0.024)	1760 (0.021)	1723 (0.021)	1686 (0.030)
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	620	1162	1461	1573	1449
Restraints / parameters	0/75	0/94	0/104	0/103	0/123
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.037/0.097	0.030/0.070	0.030/0.079	0.028/0.070	0.035/0.095
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.046/0.104	0.035/0.073	0.039/0.082	0.031/0.072	0.042/0.098
Goodness of fit	1.09	1.06	1.08	1.05	1.03
<i>Δρ</i> _{max/min} /e Å ^{−3}	1.38/−0.81	0.24/−0.25	0.27/−0.24	0.34/0.31	0.19/−0.17

2.1. Bis(amminsilver(I)) 5,5'-Azotetrazolate (1)

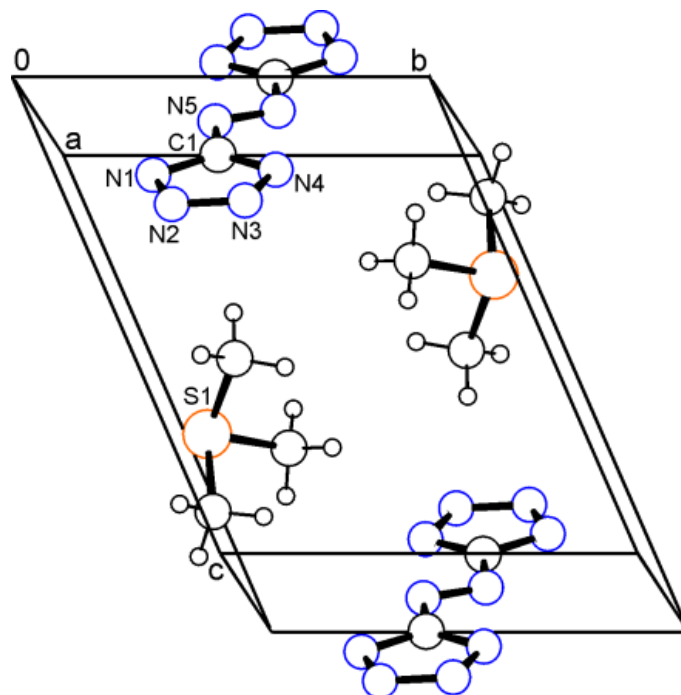
The silver ion in compound **1** coordinates to two nitrogen atoms of two azotetrazolate anions and to the ammonia molecule. Short contacts observed are Ag...N1 (2.255(5) Å), Ag...N2ⁱ (2.342(5) Å), and Ag...N6 (2.205(6) Å), respectively (Figure 1). Symmetry operation *i*: 1/2 − *x*, 1/2 + *y*, 1/2 − *z*. These interionic contacts assemble a layer structure parallel to the *bc*-plane.

Figure 1. Packing diagram of Ag salt **1**. Dashed lines represent the Ag...N interactions. Layers are arranged parallel to the *bc*-plane.



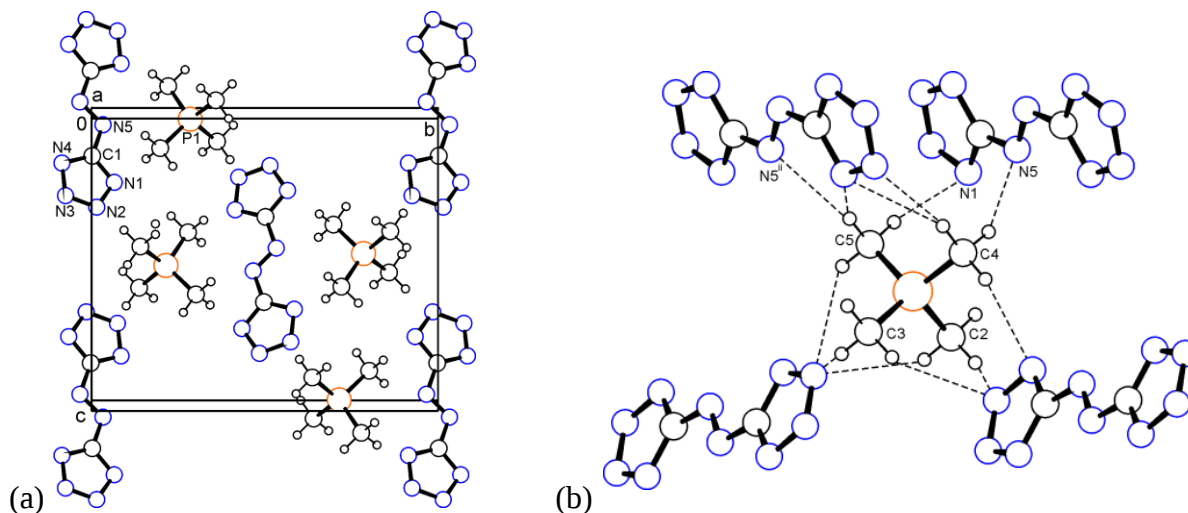
2.2. Bis(trimethylsulfonium) 5,5'-Azotetrazolate (2)

In contrast, no directional interactions are found in salt **2**. This aggregate consists of discrete ions and is predominantly stabilized by electrostatic forces. The (CH₃)₃S⁺ cation is pyramidal and exhibits approximately 3*m* symmetry as found in other trimethylsulfonium salts in the literature [32]. The C–S bond lengths are equal within the experimental error (1.782(2) Å), and the C–S–C angles differ only slightly (100.3, 101.6 and 102.4°). As discussed previously [33], the electron lone pair is not a structure-determining factor. The shortest distance between neighbouring S atoms is 3.742 Å. The unit cell is shown in Figure 2.

Figure 2. Packing diagram of trimethylsulfonium salt 2.

2.3. Bis(tetramethylphosphonium) 5,5'-Azotetrazolate (3)

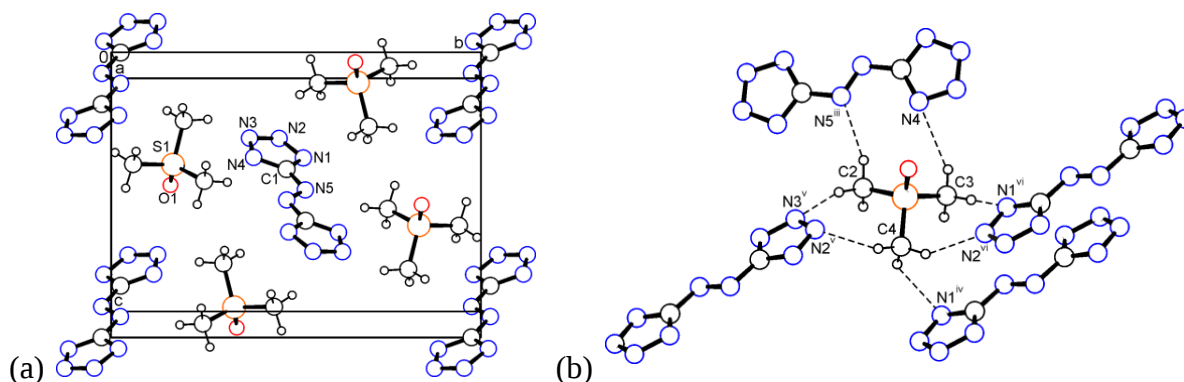
The $(\text{CH}_3)_4\text{P}^+$ cation in **3** shows only small deviations from ideal tetrahedral geometry. The C–P bond lengths range from 1.772 to 1.777 Å, and the C–P–C angles from 107.9 to 110.4°. The shortest distance between neighbouring P atoms is 5.736 Å. The crystal packing is shown in Figure 3a. There is a number of weak C–H $\cdots$ N contacts in this structure with three of them being considerably shorter than the sum of van der Waals radii. Thus, C4–H $\cdots$ N5 ($d(\text{H}\cdots\text{A}) = 2.494$ and $d(\text{D}\cdots\text{A}) = 3.404$ Å, $\angle(\text{D–H}\cdots\text{A}) = 154.4^\circ$), C5–H $\cdots$ N1 (2.566 and 3.540 Å, 172.4°), and C5–H $\cdots$ N5ⁱⁱ (2.517 and 3.403 Å, 150.2°) are the major interactions (Figure 3b). Symmetry operation ii: $-1 + x, y, z$.

Figure 3. (a) Packing diagram of tetramethylphosphonium salt 3. (b) Dashed lines represent the C–H $\cdots$ N contacts. Only N atoms engaged in major interactions are numbered.

2.4. Bis(trimethylsulfoxonium) 5,5'-Azotetrazolate (4)

The $(\text{CH}_3)_3\text{SO}$ cation in **4** again adopts a pyramidal geometry. It has neither a mirror plane nor a rotation axis. Nevertheless, the $3m$ symmetry is approximately fulfilled in good agreement with known trimethylsulfoxonium salts [34]. The shortest S–S distance is 5.245 Å. The packing is presented in Figure 4a. Probably due to the enhanced dipolar character of this cation, it participates in a series of significant C–H $\cdots$ N interactions with the anion. All nitrogen atoms of the anion serve as acceptors building a three-dimensional network (Figure 4b): C3–H $\cdots$ N4 (2.477 and 3.289 Å, 140.0°), C2–H $\cdots$ N5ⁱⁱⁱ (2.411 and 3.352 Å, 160.8°), C4–H $\cdots$ N1^{iv} (2.634 and 3.407 Å, 136.1°), C2–H $\cdots$ N3^v (2.497 and 3.428 Å, 158.6°), C4–H $\cdots$ N2^v (2.563 and 3.499 Å, 159.8°), C3–H $\cdots$ N1^{vi} (2.435 and 3.334 Å, 152.3°), C4–H $\cdots$ N2^{vi} (2.446 and 3.320 Å, 148.4°). Symmetry codes iii: $1 - x, 1 - y, 1 - z$; iv: $1/2 - x, -1/2 + y, 1/2 - z$; v: $-1/2 + x, 1/2 - y, 1/2 + z$; vi: $3/2 - x, -1/2 + y, 1/2 - z$.

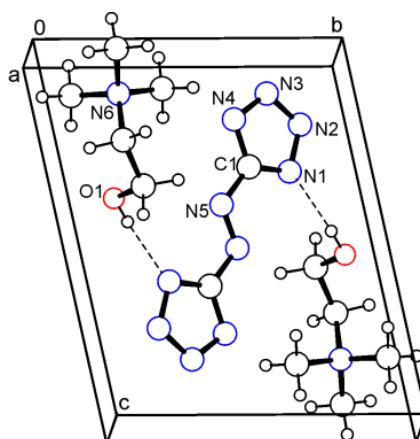
Figure 4. (a) Packing diagram of trimethylsulfoxonium salt **4**. (b) Dashed lines represent the short C–H $\cdots$ N contacts (for symmetry operators see text).



2.5. Bis(2-(hydroxyethyl)trimethylammonium) 5,5'-azotetrazolate (5)

In the structure of **5**, a strong hydrogen bond with the parameters O1–H $\cdots$ N1 (1.984 and 2.791 Å, 160.8°) between the cation and the dianion is observed. Figure 5 shows the unit cell of **5**.

Figure 5. Packing diagram of cholinium salt **5**. Dashed lines represent the strong inter-molecular O–H $\cdots$ N hydrogen bonds.



3. Experimental Section

The starting materials were obtained from Sigma-Aldrich and used as received. The NMR spectra were recorded with a Bruker AC 300 spectrometer. IR spectra were obtained with a Nicolet 5700 FT instrument in ATR mode. The impact and friction sensitivity of silver salt **1** was determined by the BAM drophammer (method 1 of 6) [35–37] and BAM friction tester [35–37] respectively. The sensitivity towards electrostatic discharge was measured using an OZM small scale electrostatic discharge device [38]. X-Ray diffraction data were collected on Oxford Diffraction Gemini-R Ultra and Nonius Kappa CCD diffractometers using Mo- $K\alpha$ radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 [39,40]. CCDC 846911-846915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

3.1. Bis(amminsilver(I)) 5,5'-Azotetrazolate (**1**)

Caution: this compound is a primary explosive with extremely high sensitivities towards friction and also electrostatic discharge when dry. Proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used during the handling of this compound. Concentrated NH_3 (2 mL) was layered over a solution of AgNO_3 (51 mg, 0.30 mmol) in H_2O (2 mL) and concentrated NH_3 (1 mL). A solution of sodium azotetrazolate pentahydrate (45 mg, 0.15 mmol) in H_2O (5 mL) and concentrated NH_3 (1 mL) was added cautiously on top of the mixture. The mixture was set aside, and orange-red crystals grew overnight at 20 °C. Yield: 10 mg (16%). No melting below 230 °C (dec). No NMR spectra could be recorded due to insolubility in common solvents. IR (neat, cm^{-1}): 1396 (s), 1214 (w), 1184 (m), 1168 (m), 1049 (w), 1032 (w), 765 (m), 737 (s), 719 (m). BAM drophammer: 2 J. BAM friction tester (<5 N). ESD: 5 mJ.

3.2. Preparation of 5,5'-Azotetrazolates (**2–5**) (General Procedure)

Ag_2SO_4 (78 mg, 0.25 mmol) was added to a solution of the respective organic halide (0.50 mmol) in H_2O (10 mL). The mixture was stirred at 50 °C for 10 min and ultrasonicated for 5 min. Subsequently, the precipitate was removed by centrifugation. Barium azotetrazolate pentahydrate (94 mg, 0.24 mmol) was added to the supernatant, and the mixture was again stirred at 50 °C for 10 min and ultrasonicated for 5 min. After centrifugation, the supernatant solution was brought to dryness in a rotary evaporator, the temperature not exceeding 50 °C. The yellow residue was recrystallized from MeOH, collected by filtration and vacuum-dried.

3.3. Bis(trimethylsulfonium) 5,5'-Azotetrazolate (**2**)

Yield: 61 mg (80%), m.p. 155 °C (dec.). ^1H NMR (DMSO-d_6 , 300 MHz): δ 2.90 (s). ^{13}C NMR (DMSO-d_6 , 75 MHz): δ 26.2 (3C), 173.3. IR (neat): ν 2992 (m), 2976 (m), 1417 (w), 1401 (s), 1196 (w), 1163 (w), 1039 (s), 773 (m), 739 (s), 733 (s) cm^{-1} .

3.4. Bis(tetramethylphosphonium) 5,5'-Azotetrazolate (3)

Yield: 70 mg (84%), m.p. 215 °C (dec.). ^1H NMR (DMSO- d_6 , 300 MHz, ppm): δ 1.85 (d, $J_{\text{H-P}} = 15.4$ Hz). ^{13}C NMR (DMSO- d_6 , 75 MHz, ppm): δ 8.9 (d, $J_{\text{C-P}} = 55$ Hz, 4C), 173.4. IR (neat, cm^{-1}): ν 2985 (m), 2915 (w), 1434 (m), 1374 (m), 1289 (m), 1174 (w), 1149 (w), 1015 (m), 973 (s), 772 (m), 725 (m).

3.5. Bis(trimethylsulfoxonium) 5,5'-Azotetrazolate (4)

Yield: 75 mg (89%), m.p. 192–193 °C (dec.). ^1H NMR (DMSO- d_6 , 300 MHz, ppm): δ 3.92 (s). ^{13}C NMR (DMSO- d_6 , 75 MHz, ppm): δ 39.2 (3C), 173.2. IR (neat, cm^{-1}): ν 2959 (s), 2878 (m), 1403 (s), 1225 (s), 1036 (s), 950 (s), 756 (m), 741 (m).

3.6. Bis(2-(hydroxyethyl)trimethylammonium) 5,5'-Azotetrazolate (5)

Yield: 65 mg (73%), m.p. 126–129 °C. ^1H NMR (DMSO- d_6 , 300 MHz, ppm): δ 3.15 (s, 9H), 3.45 (m, 2H), 3.82 (m, 2H), 5.76 (s, 1H). ^{13}C NMR (DMSO- d_6 , 75 MHz, ppm): δ 53.2 (3C), 55.1, 66.9, 173.3. IR (neat, cm^{-1}): ν 3177 (w), 3028 (w), 2902 (w), 1471 (m), 1384 (s), 1338 (w), 1179 (w), 1146 (w), 1095 (s), 1028 (w), 950 (s), 875 (m), 722 (m).

4. Conclusions

A large number of crystalline azotetrazolates is known today and can also be found in a recently published review article [41]. This versatile dianion grants access to an almost unlimited diversity of intriguing structures. Certainly, the five new salts presented in this work will be succeeded by others in due course, stimulating both materials science and crystallography. Silver salt **1** was characterized to be a thermally stable primary explosive which detonates in flame. The sensitivities towards outer stimuli are in the range of those observed for lead azide.

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