

## Salts of 5,5'-Azotetrazolate

Anton Hammerl,<sup>[a]</sup> Gerhard Holl,<sup>[b]</sup> Thomas M. Klapötke,<sup>\*[a]</sup> Peter Mayer,<sup>[a]</sup>  
Heinrich Nöth,<sup>[a]</sup> Holger Piotrowski,<sup>[a]</sup> and Marcus Warchhold<sup>[a]</sup>

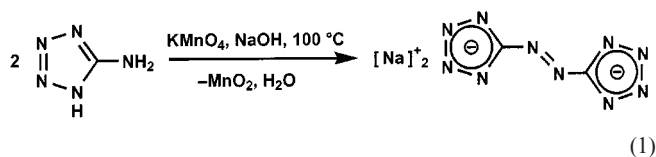
**Keywords:** Azo compounds / Hydrates / Nitrogen heterocycles / Tetrazoles / Highly energetic materials

Salts of 5,5'-azotetrazolate with alkali metal, alkaline earth metal and several trivalent cations were synthesized as potential initial explosives. The synthesis in water yields hy-

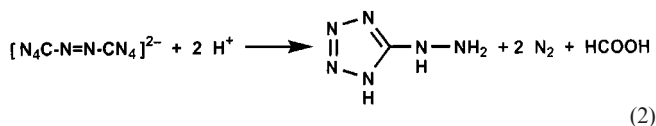
drates of these salts that were studied by NMR and vibrational spectroscopy as well as X-ray diffraction. Their thermal properties were studied by DSC and TG.

## Introduction

Thiele first prepared sodium 5,5'-azotetrazolate (**2**), which is the starting material for all other 5,5'-azotetrazolate compounds, from the oxidation of aminotetrazole with potassium permanganate [Equation (1)].<sup>[1]</sup>



He prepared several salts with metal cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Pb}^{2+}$ ) and salts of protonated nitrogen bases ( $\text{NH}_4^+$ ,  $\text{NH}_3\text{OH}^+$ ,  $\text{N}_2\text{H}_6^+$ ). 5,5'-Azotetrazolate salts decompose in mineral acid solution to form hydrazinotetrazole, dinitrogen and formic acid [Equation (2)].



Azidotetrazole,<sup>[2]</sup> 5-azo(diazomethano)tetrazole hydrate<sup>[3]</sup> and other compounds<sup>[4]</sup> were recovered as intermediates from the decomposition reaction of 5,5'-azotetrazol-

ate salts in acidic media. Salts of 5,5'-azotetrazolate with protonated nitrogen bases (e.g. guanidinium, triaminoguanidinium and hydrazinium 5,5'-azotetrazolate) are powerful gas generation agents and can be used in gas generators for airbags and fire extinguishing systems.<sup>[5]</sup> Heavy metal salts of 5,5'-azotetrazolate, especially  $\text{Pb}_2(\text{OH})_2\text{C}_2\text{N}_{10}$ , which consists of PbO ladders with a pyramidal coordination of the lead atom,<sup>[6]</sup> have been used as initiators.<sup>[7]</sup> Anhydrous sodium and potassium 5,5'-azotetrazolate are very sensitive to shock and friction.<sup>[5c,7f]</sup> 1,1'-Dimethyl-5,5'-azotetrazole, first studied by Stolle,<sup>[8]</sup> has been used as an additive in solid rocket propellants.<sup>[9]</sup> Although some of the alkali- and alkaline earth metal salts of 5,5'-azotetrazolate have been known since 1898, no data on these compounds have been reported. We therefore investigated these salts as potential initiators. We also investigated the 5,5'-azotetrazolate salts of trivalent and tetravalent cations. All 5,5'-azotetrazolate salts include water of crystallisation. We also examined the thermal properties of the compounds and determined the temperatures of water loss. For a better understanding of the decomposition of 5,5'-azotetrazolate we synthesized the free acid 5,5'-azotetrazole. The tetraphenylarsonium salt and the covalent 2,2'-dimethyl-5,5'-azotetrazolate were synthesized to investigate 5,5'-azotetrazolate units that have no interactions with cations in the solid state. The quality of all elemental analyses suffers because of the difficulty of obtaining correct values for compounds with extremely high nitrogen content.<sup>[9]</sup>

## Results and Discussion

## Syntheses and properties

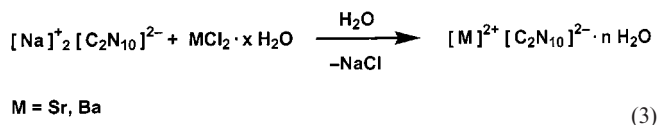
Sodium 5,5'-azotetrazolate (**2**) was used as starting material and was synthesized according to Thiele [see Equation (1)].<sup>[1d]</sup> Strontium (**8**) and barium 5,5'-azotetrazolate (**9**) were prepared from solutions of **2** and the respective

[‡] Crystal structure analyses

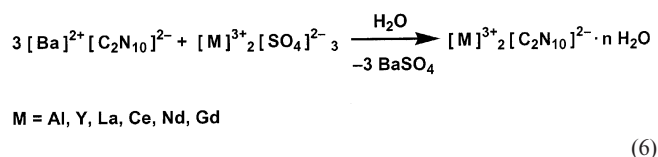
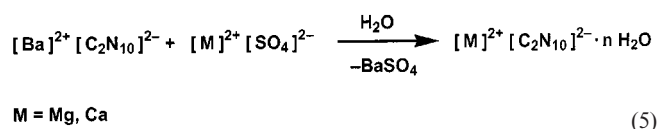
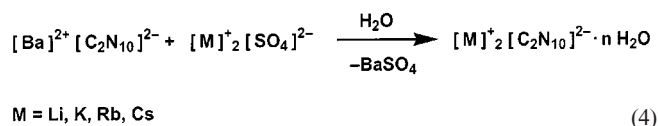
[a] Department of Chemistry, Ludwig-Maximilians-Universität München, Butenandtstr. 5–13, 81377 München, Germany  
Fax: (internat.) +49-(0)89/2180 7492  
E-mail: Thomas.M.Klapoetke@cup.uni-muenchen.de

[b] Wehrwissenschaftliches Institut für Werk-, Explosiv- und Betriebsstoffe, Großes Cent, 53913 Swisstal, Germany

metal chlorides [Equation (3)]. Both compounds are almost insoluble in water and precipitated after the solutions were mixed.



All other metal salts were obtained from the respective metal sulfates and barium 5,5'-azotetrazolate [Equation (4)–(6)]. After barium sulfate had been filtered off and the water evaporated, yellow crystals of the salts were obtained. During the reaction of  $\text{Ce}(\text{SO}_4)_2$  with barium 5,5'-azotetrazolate (**9**) a gas was evolved and no 5,5'-azotetrazolate salt of  $\text{Ce}^{\text{IV}}$  could be isolated. The  $\text{Ce}^{\text{III}}$  salt **13** does not show this decomposition.

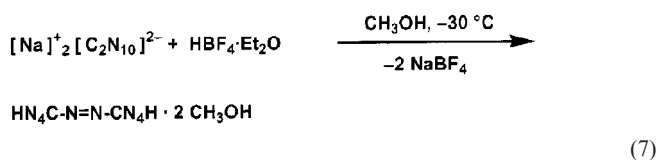


All compounds contain water of crystallisation (see Table 1). For the heavier elements the deviation of the elemental analysis is too big to calculate the exact number of water molecules present. During storage all compounds lose water; this takes place over a period of hours for the lithium **1** and potassium salt **3** as well as the salts of the trivalent cations **10**–**15**. The water loss from the other compounds takes between days and weeks. Upon loss of water, the salts of the trivalent cation **10**–**15** decompose to colourless substances. The magnesium salt **6** shows a similar behaviour. This decomposition is the reason for the low yields in the syntheses of these compounds, and it occurs due to the acidity of the metal-water complexes of the trivalent cations [cf. the decomposition of 5,5'-azotetrazolate in acidic medium, Equation (1)].

Table 1. Numbering scheme for metal salt hydrates of 5,5'-azotetrazolate

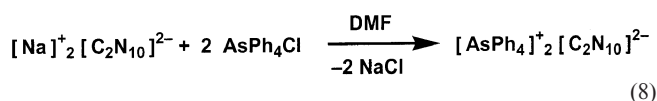
<b>1</b> $\text{Li}_2[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_6$	<b>2</b> $\text{Na}_2[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_5$	<b>3</b> $\text{K}_2[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_5$	<b>4</b> $\text{Rb}_2[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})$	<b>5</b> $\text{Cs}_2[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_2$
<b>6</b> $\text{Mg}[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_8$	<b>7</b> $\text{Ca}[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_8$	<b>8</b> $\text{Sr}[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_6$	<b>9</b> $\text{Ba}[\text{C}_2\text{N}_{10}](\text{H}_2\text{O})_5$	<b>10</b> $\text{Al}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_x$
<b>11</b> $\text{Y}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_{22}$	<b>12</b> $\text{La}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_x$	<b>13</b> $\text{Ce}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_x$	<b>14</b> $\text{Nd}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_x$	<b>15</b> $\text{Gd}_2[\text{C}_2\text{N}_{10}]_3(\text{H}_2\text{O})_x$

The free acid 5,5'-azotetrazole **16** was synthesized from the sodium salt **1** and  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  in methanol [Equation (7)] in order to gain an insight into its decomposition.

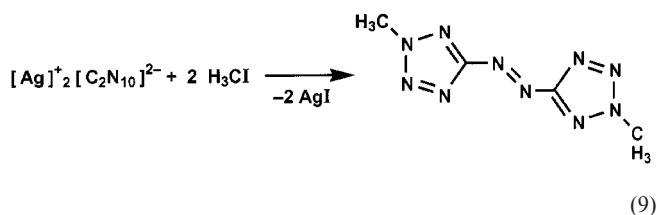


A crystal structure analysis showed the presence of two methanol molecules. The free acid is a yellow solid that can be stored for several months at  $-80^\circ\text{C}$  without decomposition.<sup>[10]</sup> At  $0^\circ\text{C}$ , however, it decomposes in an hour to form tetrazolhydrazine, and at room temperature this decomposition takes only a few seconds.

Tetraphenylarsonium 5,5'-azotetrazolate (**17**) was synthesized from the sodium salt **2** and tetraphenylarsonium chloride [Equation (8)]. The cations in this compound do not interact with the 5,5'-azotetrazole units.



We also synthesized 2,2'-dimethyl-5,5'-azotetrazolate from silver 5,5'-azotetrazolate and iodomethane [Equation (9)].



### NMR Properties

The  $^1\text{H}$  NMR spectrum of **1** shows water at  $\delta = 4.1$ ; the carbon atom of the 5,5'-azotetrazolate ion appears in the  $^{13}\text{C}$  NMR spectrum at  $\delta = 173.1$ . The  $^{14}\text{N}$  NMR spectrum of **1** in  $[\text{D}_6]\text{DMSO}$  displays no absorptions: only very concentrated solutions in  $\text{D}_2\text{O}$  (sample amount 3.5 g) show absorptions. The same sample was used for the recording of a  $^{15}\text{N}$  NMR spectrum. Figure 1 shows the broad  $^{14}\text{N}$  NMR

signals (due to the quadrupole moment of  $^{14}\text{N}$ )<sup>[11]</sup> in comparison to the sharp signals in the  $^{15}\text{N}$  NMR spectrum.

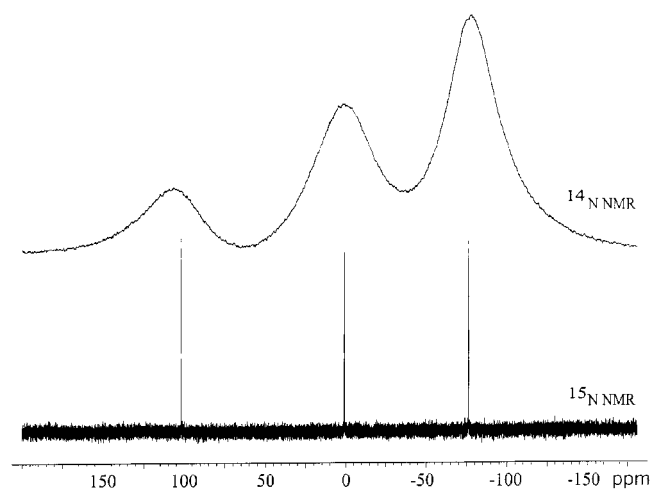


Figure 1.  $^{14}/^{15}\text{N}$  NMR spectra of **2**

The signal of the C–N nitrogen atoms of the tetrazole ring system appears at  $\delta = 2/0.6$  ( $^{14}\text{N}/^{15}\text{N}$ ), and the signal of the other two tetrazole nitrogen atoms at  $\delta = -77/-76.2$  ( $^{14}\text{N}/^{15}\text{N}$ ). The diazo nitrogen signal appears at  $\delta = 105/102.0$  ( $^{14}\text{N}/^{15}\text{N}$ ). Since the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum are the same for all 5,5'-azotetrazolate salts and the sample amount needed to record a  $^{14}\text{N}$  NMR spectrum is very high, the NMR spectra of the other salts were not recorded. The signals of the tetraphenylarsonium salt **17** in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra have the same chemical shifts as for the starting material. The signal of the methyl group of dimethylated **18** in the  $^1\text{H}$  NMR is found at  $\delta = 4.47$  ( $^{13}\text{C}$ :  $\delta = 40.5$ ), with the NH signal of the acid **16** at  $\delta = 5.68$ . The signals of the azotetrazolate carbon atoms of **16** and **18** are shifted to higher field than in the ionic compounds [ $\delta = 168.6$  (**16**) and  $171.5$  (**18**)]. No absorptions were detected in the  $^{14}\text{N}$  NMR spectra of **16** and **18**, the same as for the ionic compounds.

### Vibrational Spectra

The most intense absorptions in the IR spectra (see Table 2) are an asymmetrical C–N<sub>3</sub> stretching mode around  $1390\text{ cm}^{-1}$  and an asymmetrical C–N<sub>2</sub> stretching mode around  $735\text{ cm}^{-1}$ . For several compounds two bands are detected in this region. In the Raman spectra the most intense bands are a symmetrical C–N<sub>azo</sub> stretching mode around  $1384\text{ cm}^{-1}$  and the N–N stretching mode of the diazo group around  $1480\text{ cm}^{-1}$ . Again, for several compounds two signals are observed for these modes. The C–N<sub>azo</sub> stretching mode and the N–N stretching mode of the covalent compounds **16** and **18** are shifted slightly to higher wavenumbers relative to the 5,5'-azotetrazolate salts. Some absorptions were assigned according to a calculation of the 5,5'-azotetrazolate dianion at the B3LYP level of theory,<sup>[5d]</sup> although, due to the large number of combination

modes, especially in the IR spectra, not all modes could be assigned.

Table 2. Characteristic data for 5,5'-azotetrazolate salts (wavenumbers in  $\text{cm}^{-1}$ , Temperatures and DSC peaks in  $^{\circ}\text{C}$ )

	IR	Raman	$T_{\text{Dec.}}$	DSC
<b>1</b>	1399, 733	1484, 1387	335	64, 109, 134
<b>2</b>	1401, 732	1480, 1386	248	116, 159
<b>3</b>	1390, 727	1482, 1378	243	41, 70, 144
<b>4</b>	1395, 736	1494, 1386	239	97
<b>5</b>	1389/1382 728	1494, 1381	237	40
<b>6</b>	1393/1386 736	1499, 1375	239	–
<b>7</b>	1398 735	1496/1479 1394/1377	221	–
<b>8</b>	1396/1384 734	1488, 1382	238	76, 133
<b>9</b>	1399, 735	1488, 1391	211	129
<b>10</b>	1398, 738	1488, 1399	–	–
<b>11</b>	1403, 727	1487, 1388	–	–
<b>12</b>	1398/1384 730	1479, 1390	–	–
<b>13</b>	1408/1394, 744	1476, 1396/1388	–	–
<b>14</b>	1404/1396, 743	1477, 1394	–	–
<b>15</b>	1416, 730	1477, 1390	–	–
<b>16</b>	1383, 735	1483, 1361	–	–
<b>17</b>	1373, 742	1466, 1361	–	–
<b>18</b>	1375	1503, 1393	170	–

### Thermal Properties

The temperature for the loss of different water molecules depends on their coordination. DSC measurements (Table 2) show endotherms at temperatures between  $41^{\circ}\text{C}$  and  $144^{\circ}\text{C}$ . Compounds that have water molecules bound by hydrogen bonds lose these water molecules faster than those with the water molecules included in the coordination sphere of the cation. Slow heating ( $1^{\circ}\text{C}/\text{min}$ ) of the alkali- and alkaline earth metal salt hydrates results in an explosion at a specific decomposition temperature. The lithium salt **1** has the highest decomposition temperature of  $335^{\circ}\text{C}$ . The other alkali and alkaline earth metal salts have decomposition temperatures in the range between  $211^{\circ}\text{C}$  and  $248^{\circ}\text{C}$ , with the barium salt **9** having the lowest decomposition temperature. The salts of the trivalent cations decompose slowly at temperatures higher than room temperature: the tetraphenylarsonium salt **17** decomposes slowly at temperatures higher than  $180^{\circ}\text{C}$  and the dimethylated **18** explodes at  $170^{\circ}\text{C}$ . It is not possible to dry the compounds at higher temperatures in vacuo. All attempts resulted in explosions.

### Crystal Structures

The bonding parameters of the 5,5'-azotetrazolate anions in **1**, **2**, **4**, **7**, **9**, **11** and **15** are very similar (see Table 3) and are in agreement with the theoretical values calculated at the B3LYP/6-31+G(2df) level of theory. In the reported

Table 3. Bond lengths and angles of the 5,5'-azotetrazolate ions

	1	2	4	7	9	11 (a)	11 (b)	17	18
N(11)–N(12)	1.269(2)	1.258(3)	1.259(7)	1.255(3)	1.251(7)	1.263(4)	1.255(6)	1.081(8) 1.274(5)	1.256(3)
N(21)–N(31)	1.332(2)	1.342(3)	1.353(5)	1.336(3)	1.335(5)	1.338(4)	1.331(4)	1.324(6)	1.321(2)
N(22)–N(32)	1.336(2)	1.334(3)		1.337(3)		1.337(4)		1.340(4)	
N(31)–N(41)	1.317(2)	1.311(3)	1.319(5)	1.327(3)	1.311(6)	1.325(4)	1.322(4)	1.317(6)	1.321(2)
N(32)–N(42)	1.316(2)	1.318(3)		1.331(3)		1.326(4)		1.319(4)	
N(41)–N(51)	1.334(2)	1.344(3)	1.343(5)	1.336(3)	1.343(6)	1.332(4)	1.342(4)	1.320(6)	1.322(2)
N(42)–N(52)	1.336(2)	1.347(3)		1.334(3)		1.336(4)		1.331(4)	
N(11)–C(11)	1.398(3)	1.412(3)	1.413(5)	1.406(3)	1.414(5)	1.404(4)	1.415(4)	1.598(7)	1.411(3)
N(12)–C(12)	1.400(3)	1.406(3)		1.412(3)		1.404(4)		1.403(3)	
N(21)–C(11)	1.338(2)	1.333(3)	1.328(5)	1.341(3)	1.327(5)	1.332(4)	1.336(4)	1.322(6)	1.324(3)
N(22)–C(12)	1.345(2)	1.333(3)		1.332(3)		1.331(4)		1.343(4)	
N(51)–C(11)	1.337(2)	1.327(3)	1.336(5)	1.338(3)	1.328(5)	1.334(4)	1.329(4)	1.310(6)	1.344(3)
N(52)–C(12)	1.335(2)	1.332(3)		1.343(3)		1.332(4)		1.329(5)	
N(12)–N(11)–C(11)	112.7(2)	112.0(2)	112.7(4)	115.7(2)	112.8(4)	114.0(3)	113.1(3)	98.1(4)	112.2(2)
N(11)–N(12)–C(12)	113.3(2)	114.6(2)		112.2(2)		114.7(3)		113.0(3)	
N(21)–N(31)–N(41)	110.0(2)	109.3(2)	109.8(3)	108.9(2)	109.2(4)	120.5(3)	119.6(3)	109.6(5)	114.1(2)
N(22)–N(32)–N(42)	110.0(2)	109.2(2)		109.0(2)		120.3(3)		109.4(3)	
N(31)–N(41)–N(51)	109.4(2)	110.3(2)	109.6(3)	110.3(2)	109.8(4)	109.4(2)	110.0(3)	109.6(5)	106.4(2)
N(32)–N(42)–N(52)	109.7(2)	110.5(2)		109.9(2)		109.5(2)		110.3(3)	
N(11)–C(11)–N(21)	128.2(2)	120.6(2)	128.1(4)	117.8(2)	112.4(4)	109.6(2)	109.1(3)	111.7(4)	118.4(2)
N(12)–C(12)–N(22)	127.9(2)	118.4(2)		119.6(2)		109.4(2)		118.1(3)	
N(11)–C(11)–N(51)	120.1(2)	126.1(2)	118.3(4)	130.1(2)	128.2(4)	127.1(3)	127.9(3)	135.4(5)	127.8(2)
N(12)–C(12)–N(52)	120.0(2)	128.1(3)		128.1(2)		127.0(3)		129.0(3)	
N(21)–C(11)–N(51)	111.8(2)	113.2(2)	113.5(3)	112.13(2)	112.4(4)	112.4(3)	112.5(3)	112.9(4)	113.8(2)
N(22)–C(12)–N(52)	112.0(2)	113.4(2)		112.3(2)		112.7(3)		112.9(3)	
C(11)–N(21)–N(31)	104.3(2)	103.8(2)	103.3(3)	104.7(2)	104.7(3)	104.1(2)	104.6(3)	103.8(4)	100.9(2)
C(12)–N(22)–N(32)	104.0(2)	104.1(2)		104.8(2)		104.2(2)		103.5(3)	
C(11)–N(51)–N(41)	104.6(2)	103.3(2)	103.7(3)	104.0(2)	103.9(4)	104.5(2)	103.8(3)	104.5(5)	104.8(2)
C(12)–N(52)–N(42)	104.4(2)	102.8(2)		104.0(2)		104.2(2)		103.9(3)	

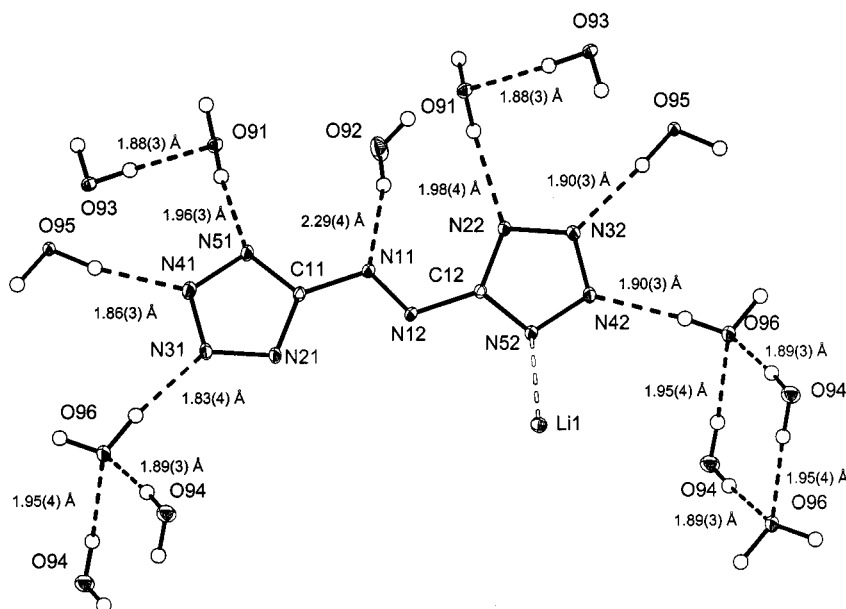


Figure 2. Coordination of the 5,5'-azotetrazolate ions in **1** (thermal ellipsoids represent 25% probability); selected bond lengths [Å]: Li(1)–O(91) 1.951(4), Li(1)–O(92) 1.951(4), Li(1)–O(93) 1.969(4), Li(1)–N(52) 2.077(4), Li(2)–O(93) 1.972(4), Li(2)–O(94) 1.910(4), Li(2)–O(95) 1.955(3), Li(2)–O(95A) 1.980(4), Li(2)–O(95A) 1.955(3); hydrogen bonds: O–N distances [Å] (OHN angles [°]), N···H distances are given in the figure: O(91)–H(911)···N(51) 2.805(3) [171(3)], O(91)–H(912)···N(22) 2.830(3) [162(2)], O(92)–H(921)···N(11) 3.188(3) [167(3)], O(93)–H(931)···O(91) 2.778(2) [176(3)], O(93)–H(932)···N(21) 2.787(3) [166(3)], O(94)–H(941)···O(96) 2.760(3) [163(3)], O(94)–H(942)···O(96) 2.700(2) [172(4)], O(95)–H(951)···N(41) 2.798(2) [169(3)], O(95)–H(952)···N(32) 2.826(3) [175(3)], O(96)–H(961)···N(42) 2.783(2) [172(3)], O(96)–H(962)···N(31) 2.793(3) [172(3)]

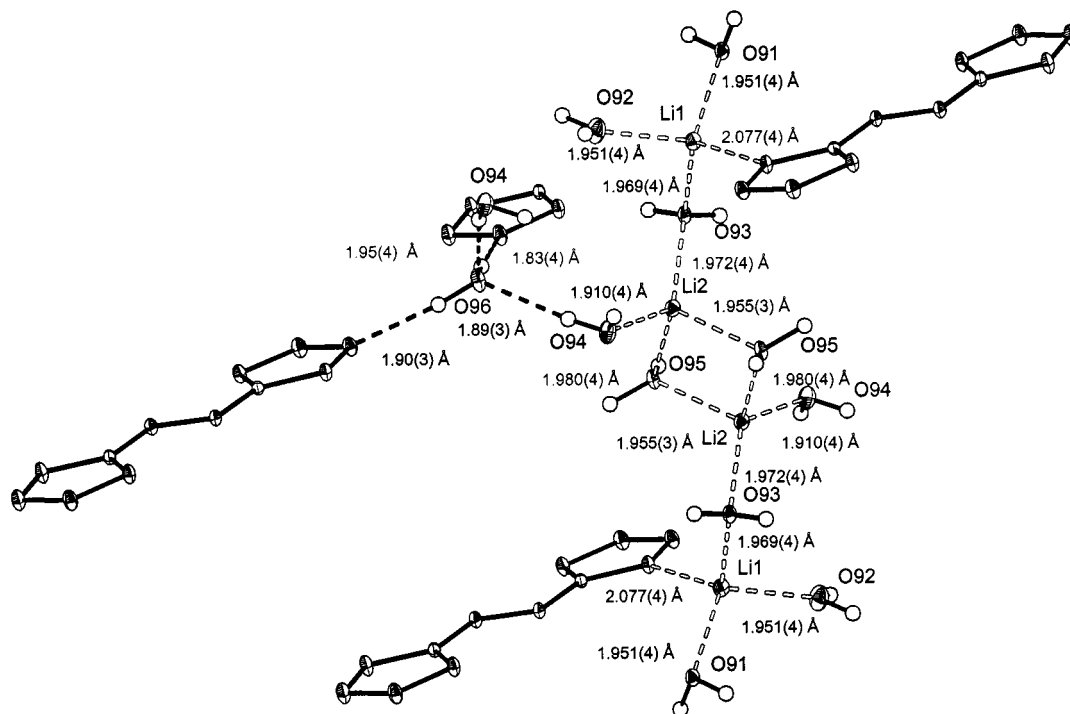


Figure 3. Coordination of the lithium ions in **1** (thermal ellipsoids represent 25% probability); parts of the 5,5'-azotetrazolate ions have been omitted for clarity

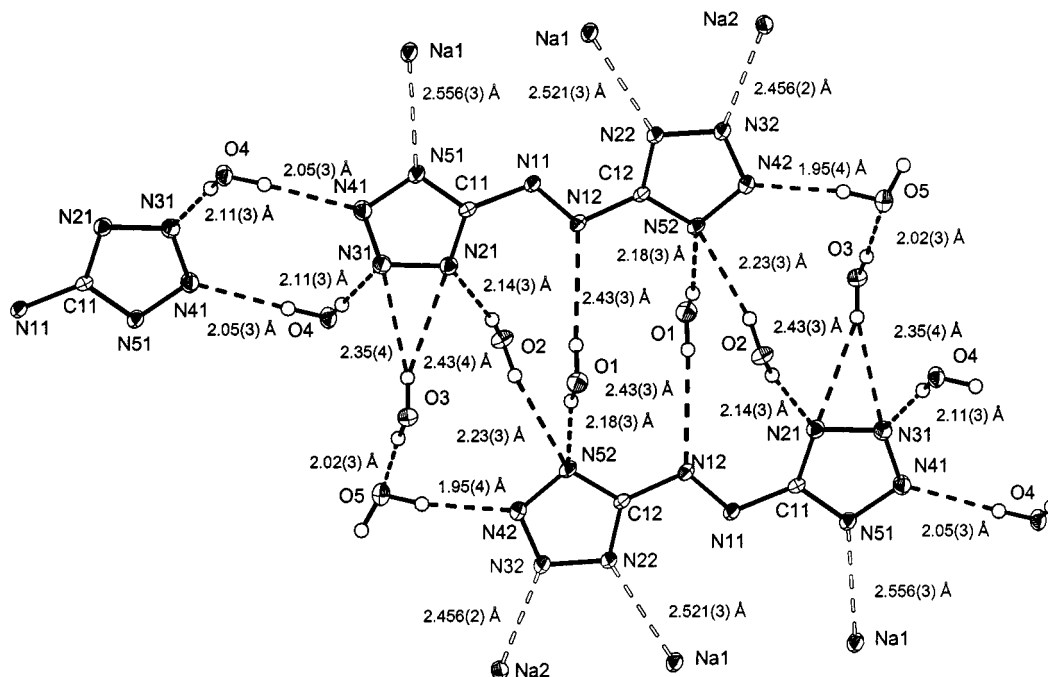


Figure 4. Coordination of the 5,5'-azotetrazolate ions in **2** (thermal ellipsoids represent 25% probability); selected bond lengths [Å]: Na(1)–O(1) 2.427(2), Na(1)–O(1A) 2.465(2), Na(1)–O(2) 2.483(2), Na(1)–O(3) 2.414(2), Na(1)–N(22) 2.521(2), Na(1)–N(51) 2.556(3), Na(2)–O(2) 2.466(2), Na(2)–O(3) 2.405(2), Na(2)–O(4) 2.376(2), Na(2)–O(4B) 2.369(2), Na(2)–O(5) 2.380(2), Na(2)–N(32) 2.456(2); symmetry operations for equivalent atoms: A:  $-x + 1, -y, -z + 1$ ; B:  $-x, -y, -z + 2$ ; hydrogen bonds: O–N and O–O distances [Å] (OHN/OHO angles [°]), N⋯H distances are given in the figure: O(1)–H(1A)⋯N(12) 3.219(3) [163(4)], O(1)–H(1B)⋯N(52) 2.973(3) [167(3)], O(2)–H(2A)⋯N(21) 2.939(3) [170(3)], O(2)–H(2B)⋯N(52) 3.039(3) [169(4)], O(3)–H(3A)⋯N(21) 3.216(3) [160(3)], O(3)–H(3A)⋯N(31) 3.156(4) [165(4)], O(4)–H(4A)⋯N(31) 2.923(3) [175(3)], O(4)–H(4B)⋯N(41) 2.859(3) [170(3)], O(5)–H(5A)⋯N(31) 3.342(3) [150(3)], O(5)–H(5B)⋯N(42) 2.776(3) [171(4)], O(3)–H(3B)⋯O(5) 2.826(3) [177(3)]

structure of dihydroxylead 5,5'-azotetrazolate<sup>[6]</sup> the N–N bond length of the diazo group is 1.20(3) Å shorter, otherwise the bonding parameters agree with the new structures.

The 5,5'-azotetrazolate ions of the lithium salt **1** are connected to water molecules through seven hydrogen bonds (see Figure 2). N(21) and N(12) are not connected to other molecules; N(52) is coordinated to a lithium ion. All other nitrogen atoms take part in hydrogen bonding to the water molecules. The hydrogen bonds to the ring nitrogen atoms have O–N distances of between 2.783(2) and 2.830(3) Å. The hydrogen bond to the N(11) nitrogen atom of the diazo group is, at 3.188(3) Å, longer. There are also hydrogen bonds between water molecules, with O–O distances of between 2.700(2) and 2.778(2) Å.

Compound **1** contains two different lithium atoms with tetrahedral coordination (Figure 3). The Li(2) atom is surrounded only by water molecules, whereas the Li(1) atom is coordinated to three water molecules and the N(52) nitrogen atom. Lithium has been reported to show tetrahedral,

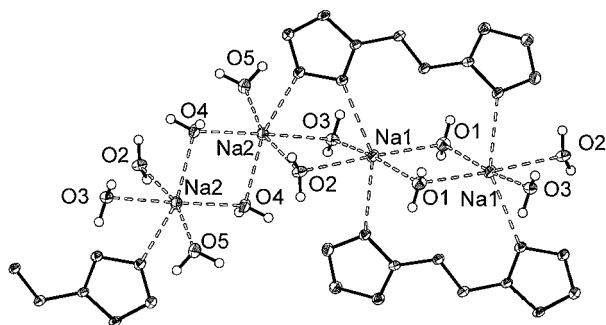


Figure 5. Coordination of the sodium ions in **2** (thermal ellipsoids represent 25% probability); parts of the 5,5'-azotetrazolate ions have been omitted for clarity

octahedral and sometimes fivefold coordination when surrounded by oxygen atoms.<sup>[12]</sup> The lithium–oxygen distances [1.910(4) to 1.980(4) Å] compare well with the reported values of 1.94–1.99 Å for tetrahedrally coordinated lithium ions. The lithium–nitrogen distance [2.077(4) Å] is also in the expected range (2.06–2.08 Å).<sup>[13]</sup> The coordination tetrahedra of two Li(2) atoms share an edge with each other and a corner with the coordination tetrahedron of Li(1) atom. The O(96) oxygen atom is not coordinated to a lithium ion, although it is bound by hydrogen bonds. The weak bonding of the O(96) oxygen atom explains the rapid loss of water from **1**.

The 5,5'-azotetrazolate ions of **2** are coordinated to three sodium ions and eight water molecules (4). The hydrogen bonds have O–N distances of between 2.776(3) and 3.342(3) Å, the longest distances belonging to the bridging hydrogen bonds of the hydrogen atoms of O(3) with N(21) and N(31). The O–N distance to the N(12) nitrogen atom of the diazo group is also longer, and there is only one hydrogen bond between water molecules [O–O distance 2.826(3) Å].

The sodium ions in **2** have different surroundings (Figure 5). They all have a distorted octahedral coordination geometry, with the Na(1) atom connected to four water molecules and the N(22) and N(51) nitrogen atoms, and the Na(2) atom to five water molecules and the N(32) nitrogen atom. The Na–O distances [2.369(2) and 2.483(2) Å]<sup>[14]</sup> as well as the Na–N distances [2.456(2) to 2.556(3) Å]<sup>[15]</sup> are in the expected range. The coordination octahedra of the sodium ions are connected edgewise. The aquated sodium ions form chains, and the 5,5'-azotetrazolate ions form stacks between these chains.

Compound **4** has an inversion centre (Figure 6) and the water molecules are hydrogen bonded to the N(3) and N(4)

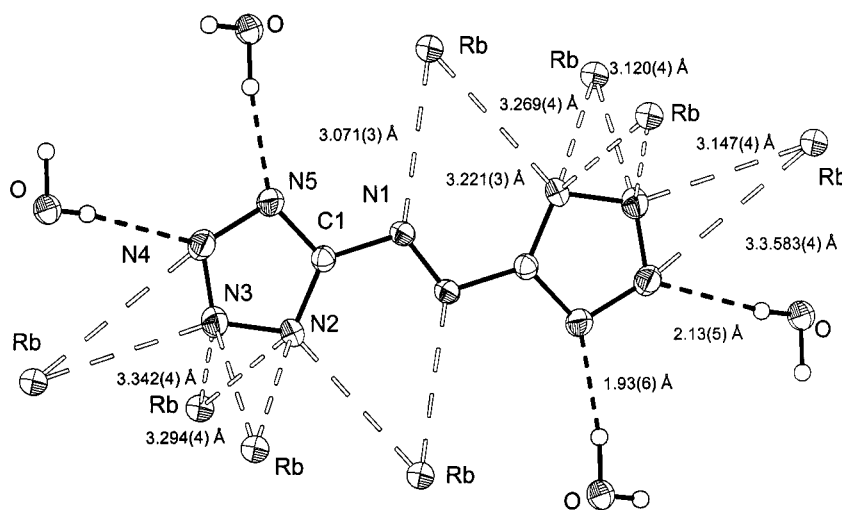


Figure 6. Coordination of the 5,5'-azotetrazolate ions in **4** (thermal ellipsoids represent 25% probability); selected bond lengths [Å]: Rb–O 2.964(3), Rb–O(B) 3.080(3), Rb–O(D) 3.125(3), Rb–O(F) 3.080(3), Rb–N(1A) 3.071(3), Rb–N(2) 3.221(3), Rb–N(2B) 3.294(4), Rb–N(2C) 3.269(4), N(2)–Rb(F) 3.294(3), Rb–N(3B) 3.342(4), Rb–N(3C) 3.120(4), Rb–N(3E) 3.147(4), N(3)–Rb(F) 3.342(4), Rb–N(4E) 3.583(4); symmetry operations for equivalent atoms: A:  $-x + 1, -y + 1, -z + 1$ ; B:  $x + 1, y, z$ ; C:  $-x + 1, -y + 1, -z + 2$ ; D:  $-x + 1, -y, -z + 2$ ; E:  $-x, -y + 1, -z + 2$ ; F:  $x - 1, y, z$ ; hydrogen bonds: O–N distances [Å] (OHN angles [°]), N...H distances are given in the figure: O–H(1)···N(5) 2.875(4) [161(5)], O–H(2)···N(4) 2.823(5) [172(6)]

nitrogen atoms [O–N distances 2.875(4) and 2.823(5) Å]. The 5,5'-azotetrazolate ions are coordinated to eight rubidium ions, with every nitrogen atom either being hydrogen bonded to a water molecule or coordinated to rubidium.

The rubidium ions in **4** are tenfold coordinated to three oxygen atoms and seven nitrogen atoms (Figure 7). The coordination polyhedra of the rubidium ions form face-sharing layers that are separated by layers of 5,5'-azotetrazolate

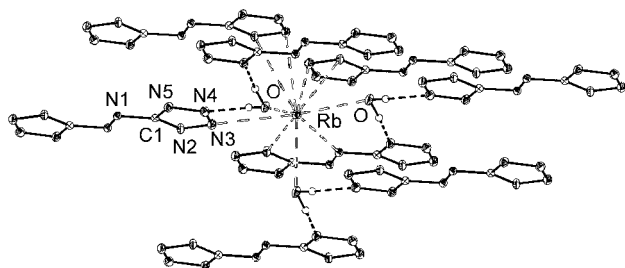


Figure 7. Coordination of the rubidium ions in **4** (thermal ellipsoids represent 25% probability); parts of the 5,5'-azotetrazolate ions have been omitted for clarity

ions. The Rb–O distances [2.964(3) to 3.125(3) Å]<sup>[16]</sup> and the Rb–N distances [3.071(3) to 3.583(4) Å]<sup>[17]</sup> agree with literature values.

The calcium ions of **7** are not coordinated to any nitrogen atoms (Figure 8). They are surrounded by eight water molecules in the form of a slightly distorted, bi-capped trigonal prism. Two coordination polyhedra share an edge. The bridging water molecules have longer Ca–O distances [2.613(2) and 2.639(2) Å] than the other water molecules [2.369(2) to 2.480(2) Å]. Calcium coordinated by eight water molecules is well-known in the literature, and the distances of the bridging and nonbridging oxygen atoms found here agree well with the previously reported values.<sup>[18]</sup> One water molecule is not connected to calcium but is hydrogen bonded to the other water molecules and to the 5,5'-azotetrazolate ions. The 5,5'-azotetrazolate ions have hydrogen bonds to eleven water molecules [O–N distances 2.787(3) to 3.226(3) Å].

The 5,5'-azotetrazolate ions of **9** are connected to six water molecules with hydrogen bonds to the N(2) and N(3) nitrogen atoms [Figure 9; O–N distances 2.791(4) to 3.158(5) Å]. The N(4) and N(5) nitrogen atoms are coordin-

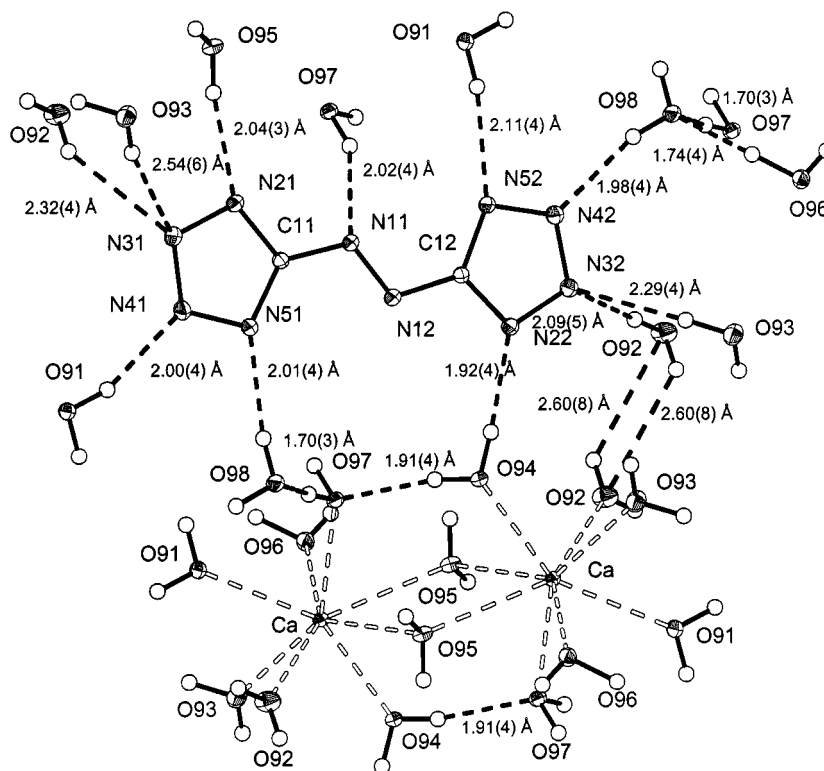


Figure 8. Structure of **7** (thermal ellipsoids represent 25% probability); selected bond lengths [Å]: Ca–O(91) 2.384(2), Ca–O(92) 2.422(2), Ca–O(93) 2.480(2), Ca–O(94) 2.369(2), Ca–O(95) 2.639(2), Ca–O(95A) 2.613(2), Ca–O(96) 2.455(2), Ca–O(97) 2.426(2); symmetry operations for equivalent atoms: A:  $-x + 1, -y + 1, -z$ ; hydrogen bonds: O–N and O–O distances [Å] (OHN/OHO angles [°]), N...H distances are given in the figure: O(91)–H(911)...N(52) 2.944(3) [170(4)], O(91)–H(912)...N(41) 2.831(3) [161(3)], O(92)–H(921)...N(32) 2.960(3) [177(4)], O(92)–H(922)...O(92) 3.145(3) [129(7)], O(92)–H(922)...N(31) 3.226(3) [148(8)], O(93)–H(931)...N(32) 3.190(3) [171(4)], O(93)–H(932)...N(31) 3.047(3) [161(4)], O(94)–H(941)...N(22) 2.787(3) [177(3)], O(94)–H(942)...O(97) 2.745(3) [169(4)], O(95)–H(951)...N(21) 2.856(3) [170(3)], O(95)–H(952)...O(96) 2.901(3) [156(4)], O(96)–H(961)...O(94) 2.959(3) [139(3)], O(96)–H(962)...O(98) 2.708(3) [164(4)], O(97)–H(971)...N(11) 2.814(3) [154(4)], O(97)–H(972)...O(98) 2.654(3) [171(3)], O(98)–H(981)...N(42) 2.804(3) [161(3)], O(98)–H(982)...N(51) 2.827(3) [166(4)]

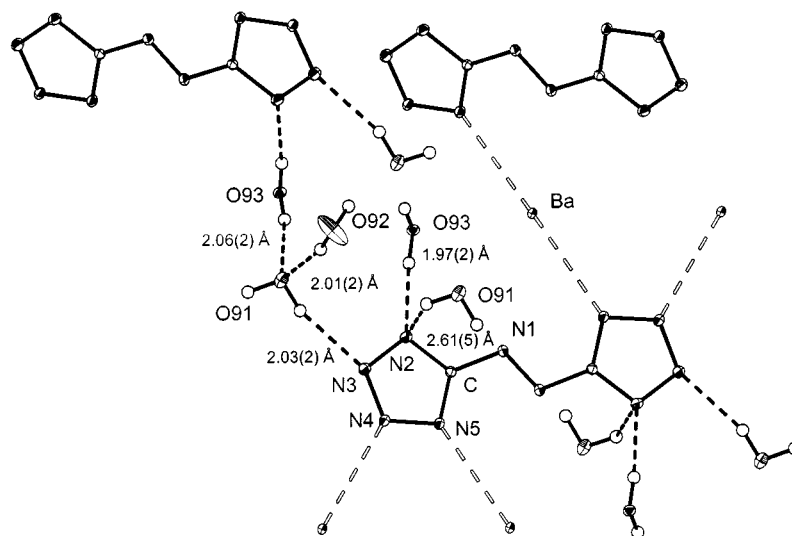


Figure 9. Structure of **9** (thermal ellipsoids represent 25% probability); selected bond lengths [ $\text{\AA}$ ]: Ba–O(92) 2.799(6), Ba–O(93) 2.840(3), Ba–O(93) 2.867(3), Ba–N(4) 3.046(4), Ba–N(5) 2.935(4); hydrogen bonds: O–N and O–O distances [ $\text{\AA}$ ] (OHN/OHO angles [ $^\circ$ ]), N $\cdots$ H distances are given in the figure: O(91)–H(911)–N(3) 2.834(6) [162(6)], O(91)–H(912)–N(2) 3.158(5) [124(5)], O(93)–H(932)–N(2) 2.791(4) [171(6)], O(92)–H(92)–O(91) 2.823(6) [167(10)], O(93)–H(931)–O(91) 2.873(4) [168(7)]

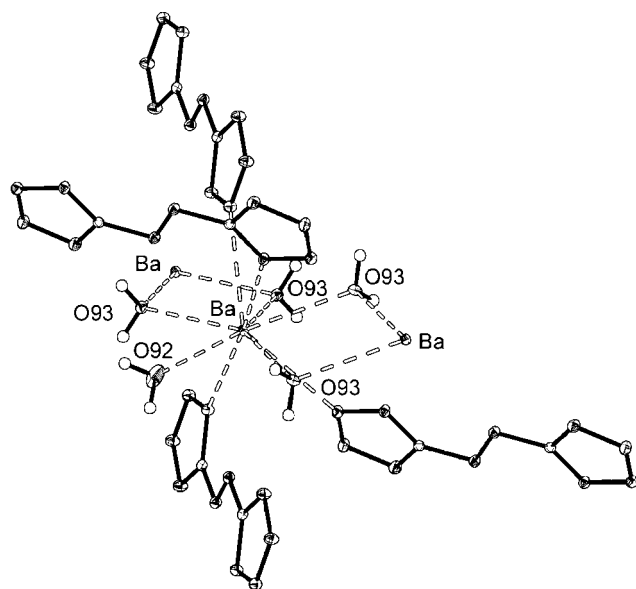


Figure 10. Coordination of the barium ions in **9** (thermal ellipsoids represent 25% probability); parts of the 5,5'-azotetrazolate ions have been omitted for clarity

ated to barium. The O(91) water molecule is not coordinated to barium, but has hydrogen bonds to the O(93) and O(92) oxygen atoms [O–O distances 2.283(6) to 2.873(4)  $\text{\AA}$ ], which are themselves coordinated to barium.

The barium atoms of **9** are coordinated to five water molecules and four nitrogen atoms to form a distorted, capped quadratic antiprism (Figure 10). The coordination polyhedra share faces. The Ba–O [2.799(6) to 2.867(3)  $\text{\AA}$ ] and

Ba–N [2.935(4) and 3.046(4)  $\text{\AA}$ ] bond lengths agree with the values for barium azide hydrate.<sup>[19]</sup> The structure consists of layers of hydrated barium atoms and a layer of stacks of 5,5'-azotetrazolate ions. The layers are connected by Ba–N interactions, explaining the greater insolubility of this compound compared to the calcium salt **7**. The insolubility of the strontium salt is probably also due to Sr–N interactions.

Compound **11** contains two different 5,5'-azotetrazolate ions, one with and one without an inversion centre (Figure 11). The bonding parameters of the two ions are identical within the standard deviation (see Table 3, **11a** and **11b**). The yttrium ions of **11**, like the calcium ions of **7**, are coordinated to eight water molecules in the form of a three-fold capped, trigonal prism. In contrast to **7**, however, the coordination polyhedra are not connected. The Y–O distances [2.322(2) to 2.450(2)  $\text{\AA}$ ] agree with those of known compounds.<sup>[20]</sup> Three further water molecules are bound with hydrogen bonds. The O–N distances of the hydrogen bonds between the water molecules and the ring nitrogen atoms of the 5,5'-azotetrazolate ions [2.722(3) and 2.973(3)  $\text{\AA}$ ] are shorter than the hydrogen bonds to the diazo nitrogen atoms [3.323(3) and 3.376(3)  $\text{\AA}$ ]. The hydrogen bonds between the water molecules have O–O distances of between 2.683(3) and 2.975(3)  $\text{\AA}$ .

The bonding parameters of the tetraphenylarsonium ions of **17** agree with the literature data.<sup>[21]</sup> The cations have no interactions with the 5,5'-azotetrazolate ions. Figure 12 shows stacks of 5,5'-azotetrazolate ions between the tetraphenylarsonium ions. The orange colour of **17** and **18**, in contrast to the yellow colour of all the other compounds, is probably due to the lack of interactions with the 5,5'-azotetrazolate unit.

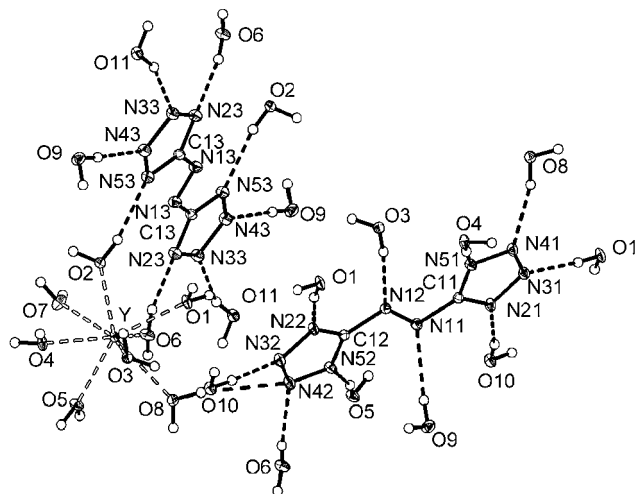


Figure 11. Structure of **11** (thermal ellipsoids represent 25% probability); selected bond lengths [Å]: Y–O(1) 2.327(2), Y–O(2) 2.361(2), Y–O(3) 2.395(2), Y–O(4) 2.351(2), Y–O(5) 2.322(2), Y–O(6) 2.340(2), Y–O(7) 2.332(2), Y–O(8) 2.450(2); symmetry operations for equivalent atoms: A:  $-x, -y + 1, -z + 1$ ; hydrogen bonds: O–N and O–O distances [Å] (NHN angles [°]): O1–H11...N22 2.845(3) [169(3)], O1–H21...N31 2.795(3) [176(4)], O2–H22...N53 2.797(3) [166(3)], O3–H23...N12 2.845(3) [173(3)], O4–H24...N51 2.820(3) [172(4)], O5–H25...N52 2.747(3) [167(4)], O6–H16...N23 2.722(3) [168(2)], O6–H26...N42 2.882(3) [163(3)], O6–H26...N52 3.323(3) [136(3)], O8–H18...N42 3.376(4) [170(3)], O8–H28...N41 2.903(3) [164(3)], O9–H19...N11 2.973(3) [162(3)], O9–H29...N43 2.773(4) [177(4)], O10–H110...N21 2.863(3) [169(3)], O10–H210...N32 2.797(3) [176(4)], O11–H211...N33 2.846(3) [159(4)], O2–H12...O9 2.757(3) [158(4)], O3–H13...O10 2.683(3) [170(3)], O4–H14...O11 2.723(3) [177(3)], O5–H15...O3 2.975(3) [173(3)], O7–H17...O11 2.747(3) [168(2)], O7–H27...O9 2.726(3) [161(3)], O11–H111...O10 2.782(3) [161(3)]

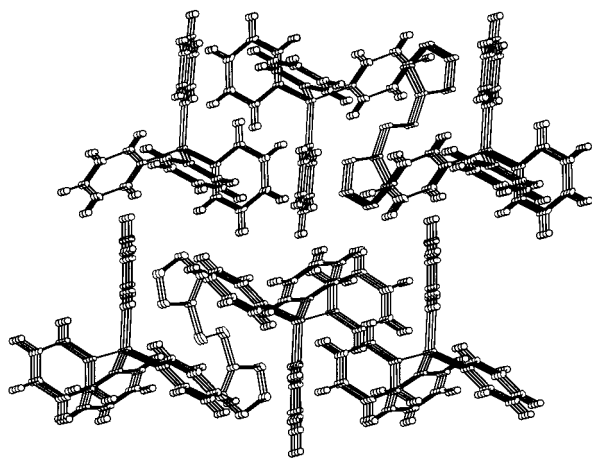


Figure 12. Stacks of 5,5'-azotetrazolate ions in **17**

The bonding parameters of **18** are in good agreement with the bonding parameters of 2-methyl-5-aminotetrazole.<sup>[22]</sup> As in **17**, the 5,5'-azotetrazole units form stacks (Figure 13).

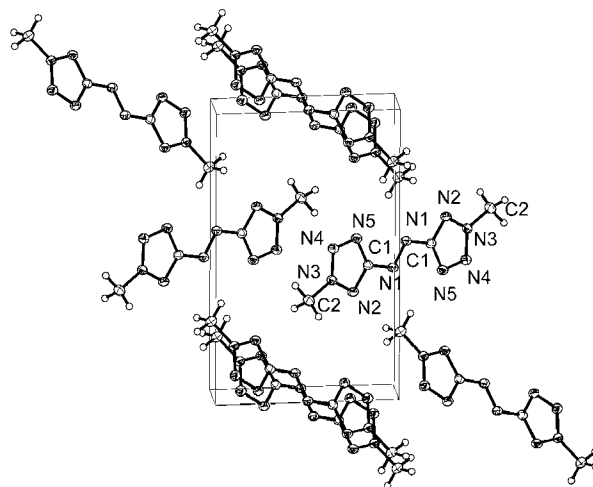


Figure 13. ORTEP plot of the unit cell of 2,2'-dimethyl-5,5'-azotetrazole **18** (thermal ellipsoids represent 25% probability); selected bond lengths [Å] and angles [°]: N(3)–C(2) 1.464(3); C(2)–N(3)–N(2) 123.0(2), C(2)–N(3)–N(4) 122.9(2)

## Conclusion

Salts of the 5,5'-azotetrazole dianion with different metal cations were examined. These salts include different amounts of water molecules that are either in the coordination sphere of the cation or bound by hydrogen bonds. The azotetrazolate ion is not connected to harder cations (calcium, yttrium), and these salts decompose, due to their acidity in water, to form tetrazolhydrazine, with evolution of nitrogen. The free acid 5,5'-azotetrazole, which was synthesized from sodium 5,5'-azotetrazolate and HBF<sub>4</sub> decomposes within seconds at room temperature, but can be handled at  $-30\text{ }^{\circ}\text{C}$ . The loss of water from the 5,5'-azotetrazolate salts occurs at different temperatures depending on how the water molecule is bound in the compound. Upon loss of water, the sensitivity of the compounds toward shock and friction increase drastically. During drying under dynamic vacuum many explosions occurred.

## Experimental Section

**CAUTION:** While all hydrates of 5,5'-azotetrazolate salts are insensitive to shock and friction, the anhydrous 5,5'-azotetrazolate salts and silver 5,5'-azotetrazolate are very sensitive. Safety equipment such as leather gloves, face shields and ear plugs are necessary.

**General Remarks:** All chemicals were used as provided from the chemical store of the Department of Chemistry. Silver 5,5'-azotetrazolate was prepared from sodium 5,5'-azotetrazolate (**2**) and silver nitrate.<sup>[14]</sup> NMR: Jeol EX 400, <sup>1</sup>H (400.0 MHz), <sup>13</sup>C (100.0 MHz): chemical shifts referenced to TMS  $\delta = 0.00$ ; <sup>14</sup>N (28.6 MHz), <sup>15</sup>N (40.5 MHz): shifts referenced to external CH<sub>3</sub>NO<sub>2</sub>. IR: Nicolet 520 FT-IR (as KBr pellets). Raman: Perkin-Elmer FTIR-2000 spectrometer (Nd-Yag Laser:

1064 nm, Laser power: 100 mW). CHN analyses: Elementar Vario EL analysator. DSC: Setaram DSC 141. TG: Setaram DTA-TG 92. MS: Balzers QMS 420.

**General Procedure:** Sodium 5,5'-azotetrazolate (**2**) was prepared following a literature synthesis.<sup>[1d]</sup> Barium (**9**) and strontium 5,5'-azotetrazolate (**8**) were synthesized by adding the respective chloride to a solution of sodium 5,5'-azotetrazolate (**2**). After stirring for 30 minutes a yellow precipitate was separated and recrystallized from water. All other 5,5'-azotetrazolate salts were obtained from the reaction of barium 5,5'-azotetrazolate (**9**) with the respective metal sulfates in water. After stirring for 30 minutes a yellow solution was obtained after filtration. The water was allowed to evaporate from this solution to give respective 5,5'-azotetrazolate salts as yellow crystals that were then recrystallized from water.

**Lithium 5,5'-Azotetrazolate Hexahydrate (1):** Yield: 92%.  $T_{\text{Dec.}} = 335^\circ\text{C}$ . DSC:  $64.0^\circ\text{C}$  (44.0 J/g),  $109.2^\circ\text{C}$  (25.0 J/g),  $133.9^\circ\text{C}$  (581.9 J/g). IR:  $\tilde{\nu} = 3425\text{ cm}^{-1}$  m, 3183 m, 1625 w, 1399 s, 1211 m, 1180 m, 1096 m, 1046 m, 891 m, 760 m, 733 s, 693 m, 602 w, 564 w. Raman:  $\tilde{\nu} = 1484\text{ cm}^{-1}$  m, 1420 w, 1387 s, 1108 m, 1080 w, 926 w, 111 w.  $\text{C}_2\text{H}_{12}\text{Li}_2\text{N}_{10}\text{O}_6$  (286.06): calcd. C 8.4, H 4.2, N 49.0; found C 11.6, H 4.1, N 82.6.

**Sodium 5,5'-Azotetrazolate Pentahydrate (2):**  $T_{\text{Dec.}} = 248^\circ\text{C}$ . DSC:  $115.6^\circ\text{C}$  (355.5 J/g),  $159.3^\circ\text{C}$  (306.1 J/g).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 4.1$  ( $\text{H}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 173.1$  ( $[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-}$ ).  $^{14}\text{N}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -77$  ( $\text{CN}_\beta$ ), 2 ( $\text{CN}_\alpha$ ), 105 ( $-\text{N}=\text{N}-$ ).  $^{15}\text{N}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -76.2$  ( $\text{CN}_\beta$ ), 0.6 ( $\text{CN}_\alpha$ ), 101.8 ( $-\text{N}=\text{N}-$ ). IR:  $\tilde{\nu} = 3612\text{ cm}^{-1}$  s, 3544 s, 3435 s, 3389 s, 3248 s, 2443 w, 2257 w, 2216 w, 2152 w, 2106 m, 1685 m, 1628 s, 1401 s, 1165 m, 1096 w, 1082 w, 1065 m, 1044 m, 776 s, 741 s, 732 s, 566 s, 526 s, 398 s. Raman:  $\tilde{\nu} = 1480\text{ cm}^{-1}$  m, 1420 w, 1386 s, 1088 m, 1058 m, 926 w, 383 w, 223 w, 123 w.  $\text{C}_2\text{H}_{10}\text{N}_{10}\text{Na}_2\text{O}_5$  (300.14): calcd. C 8.0, H 3.4, N 46.7; found C 8.1, H 3.3, N 46.6.

**Potassium 5,5'-Azotetrazolate Pentahydrate (3):** Yield: 93%.  $T_{\text{Dec.}} = 243^\circ\text{C}$ . DSC:  $40.5^\circ\text{C}$  (49.1 J/g),  $107.5^\circ\text{C}$  (70.1 J/g),  $144.1^\circ\text{C}$  (326.3 J/g). IR:  $\tilde{\nu} = 3647\text{ cm}^{-1}$  m, 3265 w, 2921 m, 2851 w, 2415 m, 2355 m, 2319 m, 2097 m, 1960 w, 1668 w, 1488 w, 1447 m, 1390 m, 1380 m, 1185 m, 1153 m, 1058 w, 1033 w, 866 m, 846 m, 822 m, 772 m, 727 s, 667 m. Raman:  $\tilde{\nu} = 1482\text{ cm}^{-1}$  m, 1416 w, 1378 s, 1189 w, 1155 w, 1079 w, 1065 w, 1053 w, 1041 w, 925 w, 736 w, 340 w, 104 w.  $\text{C}_2\text{H}_{10}\text{K}_2\text{N}_{10}\text{O}_5$  (278.32): calcd. C 7.2, H 3.0, N 42.1; found C 7.5, H 2.6, N 42.8.

**Rubidium 5,5'-Azotetrazolate Dihydrate (4):** Yield: 90%.  $T_{\text{Dec.}} = 239^\circ\text{C}$ . DSC:  $96.9^\circ\text{C}$  (200.5 J/g). IR:  $\tilde{\nu} = 3440\text{ cm}^{-1}$  s, 3281 s, 2550 w, 2509 w, 2442 w, 2103 w, 2062 w, 1981 w, 1887 w, 1791 w, 1710 m, 1519 w, 1453 w, 1395 m, 1292 w, 1199 w, 1156 m, 1073 w, 1056 w, 1033 m, 933 w, 847 w, 773 w, 736 m, 666 m, 565 m. Raman:  $\tilde{\nu} = 1494\text{ cm}^{-1}$  s, 1418 w, 1386 s, 1361 w, 1200 w, 1155 w, 1082 m, 1059 m, 1036 w, 924 w, 348 w, 104 w.  $\text{C}_2\text{H}_4\text{N}_{10}\text{O}_2\text{Rb}_2$  (371.05): calcd. C 6.4, H 1.1, N 37.7; found C 6.4, H 0.9, N 38.0.

**Caesium 5,5'-Azotetrazolate Dihydrate (5):** Yield: 91%.  $T_{\text{Dec.}} = 237^\circ\text{C}$ . DSC:  $40.3^\circ\text{C}$ . IR:  $\tilde{\nu} = 3314\text{ cm}^{-1}$  m, 3244 m, 2924 s, 2853 m, 1742 w, 1593 w, 1463 w, 1389 m, 1382 m, 1195 w, 1179 w, 1146 w, 1064 w, 1052 w, 1039 w, 773 w, 728 s, 661 w, 559 w. Raman:  $\tilde{\nu} = 1494\text{ cm}^{-1}$  s, 1467 w, 1413 w, 1381 s, 1356 w, 1313 w, 1197 w, 1154 w, 1080 w, 1068 m, 1057 m, 1035 w, 923 w, 340 w, 98 w.  $\text{C}_2\text{H}_4\text{Cs}_2\text{N}_{10}\text{O}_2$  (465.93): calcd. C 5.2, H 0.9, N 30.1; found C 5.3, H 0.8, N 29.9.

**Magnesium 5,5'-Azotetrazolate Octahydrate (6):** Yield: 15%.  $T_{\text{Dec.}} = 231^\circ\text{C}$ . IR:  $\tilde{\nu} = 3256\text{ cm}^{-1}$  s, 2881 w, 2832 w, 1668 m,

1639 m, 1529 w, 1428 w, 1393 m, 1386 m, 1323 w, 1199 w, 1053 w, 767 w, 736 m, 657 m. Raman:  $\tilde{\nu} = 1499\text{ cm}^{-1}$  m, 1452 w, 1416 w, 1375 s, 1200 w, 1086 w, 1062 m, 932 w, 112 w.  $\text{C}_2\text{H}_{16}\text{MgN}_{10}\text{O}_8$  (332.5): calcd. C 7.2, H 4.8, N 42.1; found C 7.5, H 4.4, N 34.3.

**Calcium 5,5'-Azotetrazolate Octahydrate (7):** Yield: 74%.  $T_{\text{Dec.}} = 221^\circ\text{C}$ . IR:  $\tilde{\nu} = 3513\text{ cm}^{-1}$  s, 3425 s, 3250 s, 2950 s, 2925 s, 2850 s, 2251 w, 2093 w, 1659 m, 1619 m, 1510 w, 1463 w, 1398 s, 1375 m, 1201 m, 1193 w, 1063 m, 1042 w, 943 w, 821 w, 772 w, 734 m, 672 w, 614 w, 563 w, 444 w. Raman:  $\tilde{\nu} = 1496\text{ cm}^{-1}$  m, 1479 w, 1435 w, 1416 w, 1394 s, 1377 s, 1202 w, 1089 w, 1070 s, 1051 w, 929 w, 336 w, 143 w.  $\text{C}_2\text{H}_{16}\text{CaN}_{10}\text{O}_8$  (348.29): calcd. C 6.9, H 4.6, N 40.2; found C 6.6, H 4.4, N 40.2.

**Strontium 5,5'-Azotetrazolate Hexahydrate (8):** Yield: 80%.  $T_{\text{Dec.}} = 238^\circ\text{C}$ . DSC:  $76.2^\circ\text{C}$  (51.7 J/g),  $130.3^\circ\text{C}$  (132.7 J/g),  $139.3^\circ\text{C}$  (285.6 J/g). IR:  $\tilde{\nu} = 3378\text{ cm}^{-1}$  s, 3225 s, 2967 m, 2926 m, 2844 m, 2439 m, 1651 m, 1468 w, 1396 m, 1384 s, 1258 w, 1203 w, 1161 w, 1083 w, 1068 w, 1039 w, 855 w, 802 w, 760 w, 734 w, 662 w, 554 w. Raman:  $\tilde{\nu} = 1488\text{ cm}^{-1}$  m, 1420 w, 1382 s, 1203 w, 1165 w, 1094 m, 1071 m, 1042 w, 918 w, 336 w.  $\text{C}_2\text{H}_{12}\text{SrN}_{10}\text{O}_6$  (359.80): calcd. C 6.7, H 3.4, N 38.9; found C 6.7, H 3.2, N 38.6.

**Barium 5,5'-Azotetrazolate Pentahydrate (9):** Yield: 90%.  $T_{\text{Dec.}} = 211^\circ\text{C}$ . DSC:  $129.1^\circ\text{C}$  (265.2 J/g). IR:  $\tilde{\nu} = 3401\text{ cm}^{-1}$  m, 3276 m, 3142 m, 2954 m, 2926 m, 2446 w, 2220 w, 2037 w, 1609 m, 1504 w, 1450 w, 1399 s, 1199 m, 1161 m, 1061 w, 1039 w, 805 m, 774 w, 735 m, 675 w, 562 m. Raman:  $\tilde{\nu} = 1488\text{ cm}^{-1}$  m, 1428 w, 1391 s, 1365 w, 1163 w, 1090 w, 1068 m, 1044 w, 922 w, 357 w, 206 w, 111 w.  $\text{C}_2\text{H}_{10}\text{BaN}_{10}\text{O}_5$  (391.49): calcd. C 6.1, H 2.6, 35.8 N; found C 6.3, H 3.0, N 35.3.

**Aluminium 5,5'-Azotetrazolate Hydrate (10):** IR:  $\tilde{\nu} = 2956\text{ cm}^{-1}$  s, 2845 s, 2405 m, 2400 m, 2321 m, 1601 m, 1505 w, 1489 w, 1464 w, 1442 w, 1409 m, 1398 s, 1381 w, 1228 w, 1213 w, 1190 w, 1121 w, 1085 w, 950 w, 869 w, 797 m, 738 s, 725 m, 667 w, 613 w, 553 m. Raman:  $\tilde{\nu} = 1488\text{ cm}^{-1}$  m, 1399 s, 1385 s, 1124 m, 1110 m, 1089 m, 931 w.  $\text{C}_6\text{Al}_2\text{N}_{30}\cdot(16-18)\text{H}_2\text{O}$ : found C 8.8, H 3.7, N 46.1.

**Yttrium 5,5'-Azotetrazolate Docosahydrate (11):** Yield: 24%. IR:  $\tilde{\nu} = 3598\text{ cm}^{-1}$  m, 3542 m, 3191 s, 2391 m, 1649 m, 1629 m, 1448 w, 1403 s, 1207 m, 1172 w, 1083 w, 1061 w, 1043 w, 951 w, 770 s, 727 s, 667 s, 575 m. Raman:  $\tilde{\nu} = 1487\text{ cm}^{-1}$  m, 1453 w, 1424 w, 1388 s, 1365 w, 1209 w, 1177 w, 1103 w, 1085 w, 1076 w, 1062 w, 926 w, 734 w, 356 w, 206 w, 124 w.  $\text{C}_6\text{H}_{44}\text{N}_{30}\text{O}_{22}\text{Y}_2$  (1066.53): calcd. C 6.8, H 4.2, 40.2 N; found C 8.1, H 4.2, N 40.2.

**Lanthanum 5,5'-Azotetrazolate Hydrate (12):** IR:  $\tilde{\nu} = 2954\text{ cm}^{-1}$  m, 2925 s, 2854 m, 2148 w, 1623 w, 1535 w, 1512 w, 1459 m, 1398 m, 1384 m, 1259 w, 1228 w, 1096 w, 1032 w, 968 w, 879 w, 799 w, 730 m, 630 w, 563 w. Raman:  $\tilde{\nu} = 1479\text{ cm}^{-1}$  m, 1429 w, 1390 s, 1109 w, 1088 w, 1074 w, 931 w.  $\text{C}_6\text{N}_{30}\text{La}_2\cdot(20-24)\text{H}_2\text{O}$ : found C 6.1, H 3.8, N 34.7.

**Cerium 5,5'-Azotetrazolate Hydrate (13):** IR:  $\tilde{\nu} = 3129\text{ cm}^{-1}$  m, 1624 m, 1550 w, 1529 w, 1452 w, 1408 m, 1394 m, 1361 m, 1208 w, 1184 w, 1169 w, 1048 m, 768 s, 743 s, 650 s, 627 s, 570 s. Raman:  $\tilde{\nu} = 1478\text{ cm}^{-1}$  m, 1437 w, 1396 s, 1388 m, 1110 w, 1090 w, 1073 m, 1053 w, 934 w.  $\text{C}_6\text{N}_{30}\text{Ce}_2\cdot(14-18)\text{H}_2\text{O}$ : found C 6.8, H 2.8, N 36.6.

**Neodymium 5,5'-Azotetrazolate Hydrate (14):** IR:  $\tilde{\nu} = 3138\text{ cm}^{-1}$  s, 2946 m, 2880 m, 2811 m, 2346 w, 2148 w, 1626 w, 1498 w, 1442 w, 1404 s, 1396 m, 1332 w, 1203 w, 1182 w, 1064 w, 771 m, 743 s, 730 m, 673 m. Raman:  $\tilde{\nu} = 1477\text{ cm}^{-1}$  m, 1426 w, 1394 s, 1111 w, 1091 w, 1067 m, 929 w.

**Gadolinium 5,5'-Azotetrazolate Hydrate (15):** IR:  $\tilde{\nu} = 3173\text{ cm}^{-1}$  m, 2894 w, 2146 w, 1656 w, 1541 s, 1454 s, 1416 m, 1345 m, 1221

w, 1049 w, 1022 w, 962 w, 941 w, 730 w, 681 m. Raman:  $\tilde{\nu}$  = 2935  $\text{cm}^{-1}$  w, 1488 m, 1477m, 1424 w, 1390 s, 1084 w, 1066 m, 967 w, 943 w, 680 w.

**Reaction of  $\text{Ce}(\text{SO}_4)_2$  with Barium 5,5'-Azotetrazolate:**  $\text{Ce}(\text{SO}_4)_2$  (1.00 g, 3.0 mmol) and barium 5,5'-azotetrazolate (1.81 g, 6.0 mmol) were stirred in 30 mL of water. During stirring gas evolved and a brown precipitate was formed.

**5,5'-Azotetrazole-dimethanol (16):**  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.26 g, 1.6 mmol) was added to a suspension of sodium 5,5'-azotetrazolate (**2**; 0.17 g, 0.8 mmol) in methanol. After stirring for 2 h a yellow solution was formed. The solvent was then removed in vacuo at  $-30^\circ\text{C}$  to give yellow needles of **16**, which were dried under oil-pump vacuum at  $-30^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 3.34 (s, 6 H,  $\text{CH}_3$ ), 5.68 (s, 4 H, NH, OH).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 49.9 ( $\text{CH}_3$ ), 168.6 ( $[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-}$ ). IR:  $\tilde{\nu}$  = 3518  $\text{cm}^{-1}$  m, 3224 m, 2956 m, 2923 m, 2852 m, 1687 w, 1630 w, 1467 w, 1436 w, 1383 m, 1056 s, 735 m, 666 w. Raman (100 mW,  $-30^\circ\text{C}$ ):  $\tilde{\nu}$  = 2970  $\text{cm}^{-1}$  w, 1542 m, 1483 s, 1463 w, 1361 m, 1208 m, 1122 w, 1061 w, 1003 w, 913 w, 785 w, 330 w, 180 w, 141 w, 101 w.

**Bis-tetraphenylarsonium 5,5'-Azotetrazolate (17):** Sodium 5,5'-azotetrazolate (**2**; 0.13 g (0.62 mmol) and tetraphenylarsonium chloride (0.52 g, 1.24 mmol) were stirred in 20 mL DMF for two weeks. The resulting orange solution was isolated by filtration, the DMF removed in vacuo, and the remaining orange crystals recrystallized from DMF. Yield: 435 mg (76%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 7.77–7.92 (m, PhH).  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 121.0 (C-As), 130.9 ( $\text{C}_\alpha$ ), 133.1 ( $\text{C}_\beta$ ), 134.3 ( $\text{C}_\gamma$ ). IR:  $\tilde{\nu}$  = 3421  $\text{cm}^{-1}$  m, 3158 m, 3085 m, 3047 m, 3011 m, 2228 m, 2189 w, 2158 w, 2130 s, 2101 w, 2037 m, 1998 s, 1660 m, 1578 m, 1480 s, 1438 s, 1373 m, 1338 m, 1308 m, 1282 w, 1184 m, 1171 w, 1162 w, 1081 s, 1022 w, 997 s, 931 w, 855 w, 752 s, 742 s, 723 m, 690 s, 612 w, 557 w, 521 w, 478 s, 467 s, 363 m, 351 m. Raman:  $\tilde{\nu}$  = 3061  $\text{cm}^{-1}$  m, 1578 m, 1466 m, 1397 m, 1361 s, 1019 m, 1001 m, 913 w, 672 m, 240 w, 108 w.

$\text{C}_{50}\text{H}_{40}\text{As}_2\text{N}_{10}$  (930.76): calcd. C 64.52, H 4.3, N 15.0; found C 65.8, H 4.6, N 11.1.

**2,2'-Dimethyl-5,5'-azotetrazole (18):** Iodomethane (6.05 g, 4.1 mmol) was added to a suspension of silver 5,5'-azotetrazolate (0.50 g, 1.3 mmol) in 20 mL water. The reaction mixture was stirred for three days in a closed vessel. The unreacted iodomethane was then removed in vacuo, and the reaction mixture was extracted three times with chloroform and dried with magnesium sulfate. Recrystallisation from chloroform gave 89 mg (34%) of an orange solid.  $T_{\text{Dec}}$ :  $170^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  = 4.47 (s, 6 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  = 40.5 ( $\text{CH}_3$ ), 171.5 ( $[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-}$ ). IR:  $\tilde{\nu}$  = 2928  $\text{cm}^{-1}$  m, 2857 m, 2356 w, 2347 w, 1745 w, 1457 w, 1420 w, 1375 m, 1346 m, 1316 m, 1266 w, 1189 w, 1157 w, 1094 w, 1036 w, 831 w, 774 s, 701 w, 649 w, 569 m, 556 w, 532 w, 349 m, 326 w. Raman:  $\tilde{\nu}$  = 2961  $\text{cm}^{-1}$  w, 1503 s, 1433 m, 1393 s, 1354 s, 1277 w, 1235 w, 1196 m, 1102 w, 1014 m, 914 w, 713 w.  $\text{C}_4\text{H}_6\text{N}_{10}$  (374.33): calcd. C 24.7, H 3.1, N 72.1; found C 25.0, H 3.0, 70.9 N.

**X-ray Structure Determination:** Data were collected with graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection for **2** was performed on a Siemens P4 diffractometer, for **1**, **16** and **17** on a Stoe IPDS diffractometer equipped with an image-plate area detector and for **4**, **7**, **9** and **11** on a Nonius Kappa CCD diffractometer. All data refinement was performed using SIR97<sup>[23]</sup> and SHELXL-97.<sup>[24]</sup> Acquisition and refinement data are shown in Table 4.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169910 (**1**), -169906 (**2**), -169907 (**4**), -169908 (**7**), -169911 (**9**), -169909 (**11**), -169912 (**17**), -169913 (**18**). Copies of the data can be obtained free of charge on application to CCDC, 12

Table 4. Crystallographic data and data related to data acquisition and refinement

	<b>1</b>	<b>2</b>	<b>4</b>	<b>7</b>	<b>9</b>	<b>11</b>	<b>17</b>	<b>18</b>
Chem. Formula	$\text{C}_2\text{H}_{12}\text{Li}_2\text{N}_{10}\text{O}_6$	$\text{C}_2\text{H}_{10}\text{N}_{10}\text{Na}_2\text{O}_5$	$\text{C}_2\text{H}_4\text{N}_{10}\text{O}_2\text{Rb}_2$	$\text{C}_2\text{H}_{16}\text{CaN}_{10}\text{O}_8$	$\text{C}_2\text{H}_{10}\text{BaN}_{10}\text{O}_5$	$\text{C}_6\text{H}_{44}\text{N}_{30}\text{O}_{22}\text{Y}_2$	$\text{C}_{50}\text{H}_{40}\text{N}_{10}\text{As}_2$	$\text{C}_4\text{H}_6\text{N}_{10}$
Molecular weight	286.10	300.18	371.09	348.33	391.492	1066.53	930.763	194.158
Color, Habit	yellow prism	yellow prism	yellow prism	yellow prism	yellow block	yellow prism	Orange, irregular	orange, irregular
Crystal size [mm]	$0.25 \times 0.13 \times 0.10$	$0.4 \times 0.4 \times 0.2$	$0.25 \times 0.12 \times 0.06$	$0.26 \times 0.22 \times 0.16$	$0.35 \times 0.18 \times 0.10$	$0.30 \times 0.09 \times 0.04$	$0.28 \times 0.15 \times 0.09$	$0.30 \times 0.15 \times 0.06$
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
$a$ [Å]	8.852(2)	7.1239(8)	4.41100(1)	6.52990(1)	16.3414(2)	10.1262(1)	9.4125(7)	4.5638(9)
$b$ [Å]	8.883(2)	7.5783(8)	7.7298(2)	10.05040(1)	9.4086(2)	10.3796(2)	13.509(1)	12.126(4)
$c$ [Å]	9.119(2)	12.055(1)	7.7716(2)	11.2142(2)	8.5886(2)	10.4524(1)	18.487(2)	7.807(2)
$\alpha$ [°]	88.32(2)	79.756(2)	80.780(1)	70.1999(8)	90	73.0015(9)	78.05(1)	90
$\beta$ [°]	82.48(2)	81.105(2)	84.569(1)	89.9935(7)	121.0060(9)	78.6168(9)	76.618(9)	99.97(3)
$\gamma$ [°]	61.07(2)	68.230(2)	80.303(1)	85.4095(7)	90	74.7266(6)	72.51(1)	90
$V$ [Å <sup>3</sup> ]	621.7(2)	592.0(1)	257.10(1)	689.95(2)	1131.81(4)	1004.84(2)	2157.3(3)	425.5(2)
$Z$	2	2	1	2	4	1	2	2
$\rho$ (calcd.) [mg/m <sup>3</sup> ]	1.528	1.684	2.396	1.677	2.29755	1.762	1.433	1.515
$\mu$ [mm <sup>-1</sup> ]	0.137	0.209	9.521	0.516	3.547	2.985	1.598	0.116
$F(000)$	296	308	176	364	752	544	952	200
$\theta$ range [°]	2.25 bis 28.11	3.44 bis 57.98	2.66 bis 27.44	1.93 bis 27.97	0.999 bis 27.49	2.05 bis 27.48	1.82 bis 25.91	3.14 bis 25.82
Temp. [K]	200(2)	193(2)	200(3)	200(3)	200(2)	200(2)	200(3)	200(3)
Index range	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$	$-8 \leq h \leq 8$ $-8 \leq k \leq 9$ $-15 \leq l \leq 15$	$-5 \leq h \leq 5$ $-10 \leq k \leq 10$ $-10 \leq l \leq 9$	$-8 \leq h \leq 8$ $-13 \leq k \leq 13$ $-14 \leq l \leq 14$	$-21 \leq h \leq 20$ $-12 \leq k \leq 12$ $-11 \leq l \leq 10$	$-13 \leq h \leq 13$ $-13 \leq k \leq 13$ $-13 \leq l \leq 12$	$-10 \leq h \leq 16$ $-16 \leq k \leq 16$ $-22 \leq l \leq 22$	$-5 \leq h \leq 4$ $-10 \leq k \leq 14$ $-9 \leq l \leq 9$
Refl. collected	5327	3456	3993	13112	8907	16144	17080	1570
Refl. unique	2761	1822	1161	3160	1303	4534	7814	782
Refl. observed (4 $\sigma$ )	1918	1510	1088	2766	1246	3972	5502	500
$R$ (int.)	0.0971	0.0196	0.0388	0.0346	0.0482	0.0402	0.1096	0.0455
Data/restraints/parameters	2761/0/229	1822/9/204	1161/0/81	3160/1/254	1303/7/103	3972/33/338	7814/0/559	782/0/76
GOOF	0.985	1.065	1.294	1.206	1.364	1.201	0.880	0.863
$R_1$ , $wR_2$ [ $I > 4\sigma(I)$ ]	0.0524, 0.1113	0.0431, 0.1194	0.0279, 0.0924	0.0345, 0.0986	0.0211, 0.0572	0.0310, 0.0846	0.0463, 0.0862	0.0398, 0.0776
$R_1$ , $wR_2$ (all data)	0.0754, 0.1314	0.0532, 0.1265	0.0314, 0.1122	0.0425, 0.1144	0.0260, 0.0959	0.0426, 0.1138	0.0679, 0.0920	0.0736, 0.0835
Larg. res. peak [e/Å <sup>3</sup> ]	0.357/−0.357	1.079/−0.206	0.667/−0.731	0.452/−0.349	1.609/−1.585	0.982/−0.739	1.204/−1.051	0.150/−0.171

Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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