

## Tetrazole-5-carboxylic Acid Based Salts of Earth Alkali and Transition Metal Cations

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The tetrazole-5-carboxylate anion was investigated as ligand for earth alkali metal and transition metal complexes. Therefore, the strontium **4a** (\*3H<sub>2</sub>O, \*2.75H<sub>2</sub>O, \*2.5H<sub>2</sub>O), barium **4b** (\*3H<sub>2</sub>O), copper **4c** (\*3.5H<sub>2</sub>O, \*4H<sub>2</sub>O), manganese **4d** (\*4H<sub>2</sub>O, \*5H<sub>2</sub>O), and silver tetrazol-5-carboxylate **4e** (\*1.56H<sub>2</sub>O) were synthesized and characterized by vibrational spectroscopy (IR), and the crystal structures of **4a** (\*2.75H<sub>2</sub>O, \*2.5H<sub>2</sub>O), **4b**\*3H<sub>2</sub>O, **4c**\*4H<sub>2</sub>O, and **4d**\*5H<sub>2</sub>O were determined using single crystal X-ray diffraction. The thermal stability was investigated by DSC-measurements, and the sensitivity toward impact and friction was determined by BAM-standards. The copper, strontium, and barium tetrazole-5-carboxylate proved to be suitable thermal and physical stable colorants for pyrotechnic compositions. The crystal structure of the tetragonal modification of strontium tetrazole-5-carboxylate possesses channels along the *c*-axis, leading to a porous material.

### Introduction

Tetrazoles possess a special place among nitrogen rich heterocycles. Despite their high content of nitrogen (80% for 1*H*-tetrazole), their thermal stability is astonishing high. The field of application of tetrazoles covers pharmaceutical<sup>1</sup> and biomedical applications,<sup>2</sup> as well as membranes,<sup>3</sup> anti-fogging in photographic materials,<sup>4</sup> and energetic materials.<sup>5</sup> Moreover, their diversity allows a usage as ligands in inorganic chemistry. One example for their versatility is the

[ $\mu$ -tris(1,2-bis(tetrazol-1-yl)propane-N1,N1')iron(II)] bis(perchlorate), an iron(II) chain<sup>6</sup> or [tris(1,4-bis(tetrazol-1-yl)-butane-N1,N1)iron(II)] bis(perchlorate), a three-dimensional structure<sup>7</sup> both showing spin-crossover. Another interesting class of tetrazole-containing complexes is formed by the copper nitriminotetrazoles. These compounds show weak antiferromagnetic interaction.<sup>8</sup> Beyond that, the chemistry of lanthanide tetrazolates is another proof for the versatility of the tetrazolate ligand. Examples are the formation of hydrogels of La(III) cations with 5-(2-pyridyl)tetrazolate<sup>9</sup> or potential new contrast agents based on lanthanide(III) cations and 5-(2-pyridyl)tetrazolate or 5-(2-pyridyl-1-oxide)tetrazolate<sup>10</sup> Furthermore, complexes containing cations like barium, strontium, or copper are sought components for pyrotechnical mixtures, by the combination of the energetic nitrogen rich ligand and the colorant metal cation.<sup>11</sup> Especially

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the usage of copper(II)-compounds instead of barium in green fireworks was intensively studied.<sup>12</sup> The red flame colors can be obtained either by strontium or by lithium or calcium.<sup>13</sup> In case of strontium, the red flame color is formed by the light-emitting species Sr(I)OH and Sr(I)Cl, being formed in the gas phase.<sup>14</sup>

Among energetic tetrazole containing compounds, 5-nitrotetrazolate peaks out with an oxygen balance of zero (using N<sub>2</sub> and CO<sub>2</sub> as products of decomposition<sup>15</sup>). The disadvantage of 5-nitrotetrazolates are their high sensitivity toward friction (in case of the potassium, rubidium, and cesium salt > 5 N<sup>16</sup>) and high sensitivity toward impact (in case of the hydrazine, diaminoguanidine, and triaminoguanidine salt > 4 J).<sup>17</sup> The low physical stability complicates an industrial application, despite their good properties.

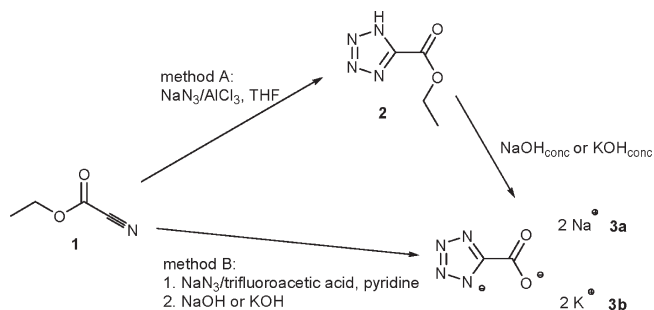
To develop similar compounds that are much more stable, the corresponding derivatives of tetrazole-5-carboxylic acid were prepared and characterized. In contrast to the nitro group of nitrotetrazolate, the carboxylic moiety of tetrazole-5-carboxylic acid can form a stable network of intermolecular interactions. Moreover, the two different points of coordination (the carboxylate moiety and tetrazolate moiety) could lead to interesting materials with new properties.

With regard to an industrial application, special interest was paid on the investigation of colorant agents for pyrotechnical compositions. Particularly in case of civil applications, physical and thermal stable colorant agents are desired for a safe handling.

## Results and Discussion

**Synthesis.** To synthesize complexes of tetrazole-5-carboxylic acid, two different ways of preparation were investigated. The first method was the synthesis of ethyl 1*H*-tetrazole-5-carboxylate (**2**) developed by Behringer.<sup>18</sup> The formed ethyl ester **2** was converted into the corresponding disodium salt of tetrazole-5-carboxylic acid (**3a**) by treatment with a concentrated solution of sodium hydroxide in hot water. In the second step, the solution was acidified to pH 1, and the desired metal nitrate was added (Scheme 1, *method A*). The second pathway was to generate directly the dipotassium salt of the tetrazole-5-carboxylic acid (**3b**) according to a European patent.<sup>19</sup> The yields of this reaction were reported with up to 99% in case of **3a** and 90% in case of the **3b**. A further investigation of the formed colorless powder revealed that it contained a varying amount between 10% to

**Scheme 1.** Methods A and B for the Synthesis of **3a** or **3b**



20% of the corresponding carbonates, a result of the decomposition of the used ethyl cyanoformate (**1**) during the reaction. Carrying out the reaction several times, only yields of 60% could be achieved (Scheme 1, *method B*). Compared with the yield of method A (10% to 15%), method B was more suitable to prepare large quantities of the tetrazole-5-carboxylate. The advantage of method A was the purity of the formed product. Instead of method B, method A yields pure product, and the formed salt can be used stoichiometrically. Compounds **3a** and **3b** of method B were always contaminated by carbonate and also contained a varying amount of crystal water. In this work, the tetrazole-5-carboxylate of method B was used because a stoichiometric usage of **3** and the desired cation was not necessary.

The synthesis of the strontium, barium, and copper tetrazole-5-carboxylate was carried out with a view to an application as colorant agents in pyrotechnics. The silver tetrazole-5-carboxylate could be used for metathesis reactions to introduce nitrogen rich cations. To convert **3a** or **3b** into the desired strontium, barium, copper, manganese, and silver salts, **3a** or **3b** were dissolved in the corresponding 2*N* mineral acid to remove residues of carbonate (in case of nitrates in nitric acid or in case of the chlorides in hydrochloric acid) and a 5-fold excess of the salt was added (Scheme 2). In case of the copper (**4c**), manganese(II) (**4d**), and silver tetrazole-5-carboxylate (**4e**), the product precipitated instantly, whereas the strontium (**4a**) and barium (**4b**) salts crystallized after some hours.

**Vibrational and NMR spectroscopy.** Compounds **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O were characterized by IR spectroscopy. A comparison between the different spectra shows the characteristic bands of the anion, along with the vibrations of the crystal water. The broadness of the band at about 3400 cm<sup>-1</sup> (OH-stretching) depends on the number of different molecules of crystal water. Compound **4d**\*4H<sub>2</sub>O possesses a strong band at 3440 cm<sup>-1</sup> with three shoulders at 3381 cm<sup>-1</sup>, 3289 cm<sup>-1</sup>, and 3171 cm<sup>-1</sup>, similar to the pattern of **4c**\*3.5H<sub>2</sub>O (strong band at 3421 cm<sup>-1</sup> with two shoulders at 3256 cm<sup>-1</sup> and 3118 cm<sup>-1</sup>). Surprisingly, the pattern of **4a**\*3H<sub>2</sub>O and **4b**\*3H<sub>2</sub>O are very different. Compound **4a**\*H<sub>2</sub>O only possesses a strong, sharp band at 3421 cm<sup>-1</sup> with two shoulders at 3565 cm<sup>-1</sup> and 3250 cm<sup>-1</sup>, whereas **4b**\*3H<sub>2</sub>O shows four equivalent bands at 3539 cm<sup>-1</sup>, 3453 cm<sup>-1</sup>, 3368 cm<sup>-1</sup>, and 3230 cm<sup>-1</sup>.

An investigation of the vibrations of the anion of **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O reveals only small differences between the different complexes (Table 1). An exception is the asymmetric valence

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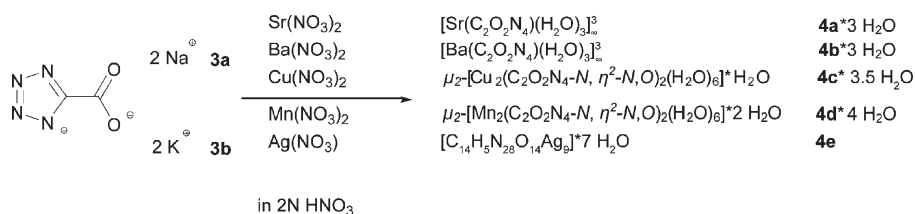
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**Scheme 2.** Synthesis of the Strontium, Barium, Copper, Manganese, and Silver Salt**Table 1.** Comparison between Selected Vibrations of **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O with the Calculated Values of the Uncoordinated C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>-Anion,<sup>a</sup> Using DFT BLYP/6-31G<sup>ab</sup>

<b>4a</b> *3H <sub>2</sub> O	<b>4b</b> *3H <sub>2</sub> O	<b>4d</b> *4H <sub>2</sub> O	<b>4e</b> *1.56H <sub>2</sub> O	<b>4c</b> *3.5H <sub>2</sub> O	free C <sub>2</sub> N <sub>4</sub> O <sub>2</sub> -anion (obtained from <b>4c</b> *3H <sub>2</sub> O)		
exp.	exp.	exp.	exp.	exp.	theory * 0.9940	theory	vibration
1622	1576	1635	1615	1661	1679	1689	$\nu_{as}(\text{COO}^-)$
1487	1490	1484	1468	1487	1409	1418	$\nu_s(\text{C}-\text{C})$
1372	1389	1382	1382	1382	1358	1366	$\delta_{as}(\text{tetrazole})$
1326	1323	1323	1323	1320	1319	1327	$\nu_s(\text{tetrazole})/\nu_s(\text{COO}^-)$
1188	1182	1179	1175	1192	1187	1194	$\nu_s(\text{tetrazole})$
1110	1054	1083	1155	1083	1055	1062	$\nu_s(\text{tetrazole})$
1067	1037	1064	1037	1054	1048	1055	$\delta_s(\text{tetrazole})$
814	830	834	811	817	802	807	$\delta_s(\text{COO}^-)$
683	703	679	693	670	704	708	$\gamma_s(\text{COO}^-)/\gamma_s(\text{tetrazole})$

<sup>a</sup> Bond distances were obtained from the crystal structure of **4c**\*3H<sub>2</sub>O. <sup>b</sup> The vibrations of the crystal water were neglected.

vibration of the carboxyl group. The band of the asymmetric valence vibration ranges from 1576 cm<sup>-1</sup> in case of the barium salt **4b**\*3H<sub>2</sub>O to 1661 cm<sup>-1</sup> of the copper salt **4c**\*3.5H<sub>2</sub>O. For being the only compound with two cations per C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>-anion, the silver salt **4e**\*1.56H<sub>2</sub>O was not considered in the discussion of the IR spectra. A comparison between selected vibrations of **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O and calculated values of the uncoordinated C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>-anion are given in Table 1.

The <sup>13</sup>C and <sup>15</sup>N NMR spectrum of the tetrazol-5-carboxylate anion was recorded using the disodium salt because the solubility of compounds **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O in any solvents was not sufficient for a NMR spectrum. To verify the assignment, the <sup>13</sup>C and <sup>15</sup>N NMR shifts were calculated using the isotropic magnetic shieldings of the GIAO (Gauge-Independent Atomic Orbital) method implemented in Gaussian03.<sup>20,21</sup> The NMR shielding tensors were

calculated at the MPW1PW91/aug-cc-pVDZ level of theory using the GIAO method.<sup>21</sup> The calculations gave a chemical shift of 165.1 ppm for the carboxyl group and 162.8 ppm for the tetrazole carbon atom. These results confirm the assignment of C5 to the signal at 160.6 ppm and C6 to the signal at 167.5 ppm. Compared to sodium 5-nitrotetrazolate (167.5 ppm, C5, acetone-*d*<sub>6</sub>),<sup>22</sup> ammonium 5-nitrotetrazolate (169.5 ppm, C5, DMSO-*d*<sub>6</sub>)<sup>23</sup> and 1*H*-imidazole-2-carboxylic acid (141.1 ppm CN<sub>2</sub>, 157.6 COOH, DMSO-*d*<sub>6</sub>), the chemical shift of the quaternary carbon atom of the tetrazole moiety is located between these compounds. In case of the <sup>15</sup>N NMR, the experimental shifts of -3.5 ppm for N2 and N3 and -67.3 ppm for N1 and N4 are in accordance with the calculated values of +10.6 ppm for N2 and N3 and -47.5 ppm for N1 and N4.

**Crystal Structures.** To investigate the different types of coordination of earth alkali salts and transition metal salts, crystals of **4a** (\*2.75H<sub>2</sub>O, \*2.5H<sub>2</sub>O), **4b**\*3H<sub>2</sub>O, **4c**\*4H<sub>2</sub>O, and **4d**\*5H<sub>2</sub>O were synthesized. In this listing, the manganese salt **4d**\*5H<sub>2</sub>O is only of academic interest because an application as colorant agent in pyrotechnics is not possible.

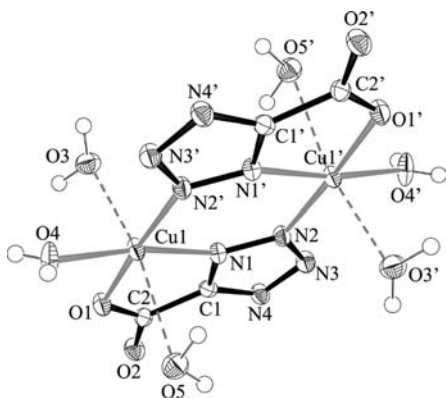
**Transition Metal Complexes.** The structures of the transition metal salts of tetrazol-5-carboxylate and copper **4c**\*4H<sub>2</sub>O and manganese **4d**\*5H<sub>2</sub>O are similar. Compound **4c**\*4H<sub>2</sub>O crystallizes in the monoclinic space-group *C2/c* with eight molecular formulas per unit cell and four molecules water per copper cation. The copper tetrazol-5-carboxylate units form dinuclear complexes, involving two copper tetrazol-5-carboxylate units and six molecules of water (Figure 1). The copper cation is

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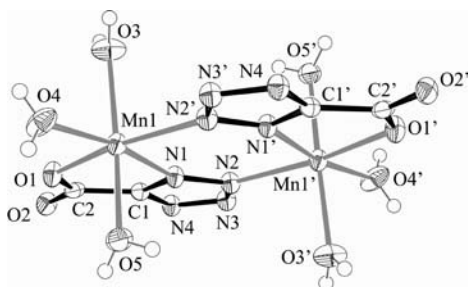
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**Figure 1.** Molecular structure of the dinuclear complex of  $4c \cdot 4H_2O$ . Thermal ellipsoids are drawn at the 50% probability level.

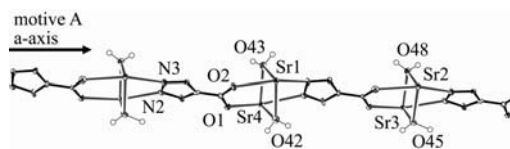


**Figure 2.** Molecular structure of the dinuclear complex of  $4d \cdot 5H_2O$ . Thermal ellipsoids are drawn at the 50% probability level.

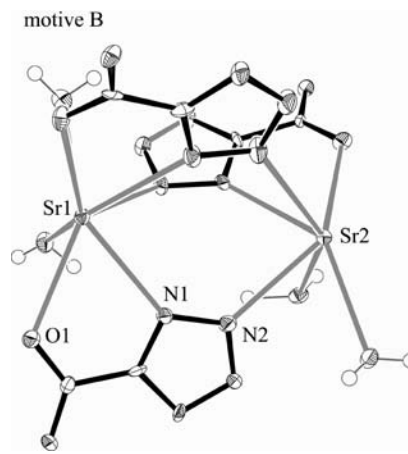
coordinated equatorial to N1 and O1 of the first, N2 of the second tetrazol-5-carboxylate anion, and to one molecule of water (O4). Two other molecules of water are coordinated axial to the copper cation (O3/O5), leading to a distorted octahedral sphere of coordination (Figure 1). The bond length of the equatorial water molecule (O4; 1.931 Å) is about 21% shorter than the bond length to the axial water molecule (O3; 2.343 Å). The bond length of the other axial molecule of water (O5) with 2.523 Å is elongated, compared to O3. The remaining molecule water (O6) is connected by several hydrogen bonds to the other water molecules and to N3.

Like  $4c \cdot 4H_2O$ ,  $4d \cdot 5H_2O$  crystallizes in the monoclinic spacegroup  $C2/c$  with eight molecular formulas per unit cell and five molecules of crystal water per manganese cation. In contrast to  $4c \cdot 4H_2O$ , the manganese cation is coordinated octahedrally without distortion by two tetrazol-5-carboxylate moieties and three molecules of water (Figure 2). The bond distances between the cation and the water molecules vary between 2.117 Å and 2.173 Å. Like the copper cation, the manganese cation is coordinated to O1 and N1 of the first and N2 of the second tetrazol-5-carboxylate anion. The molecules of crystal water have a significant part in the structure by stabilizing it with several hydrogen bonds. Three molecules of water are coordinated equatorially and axially to the manganese cation (O3, O4, and O5), whereas the last two water molecules form hydrogen bonds to the water molecules and N3.

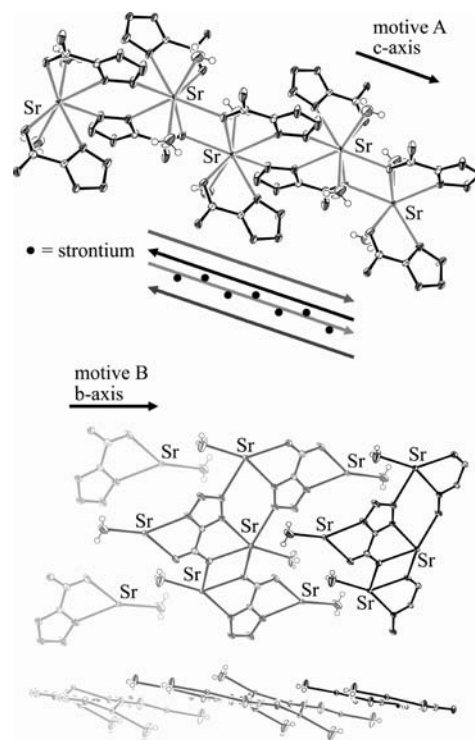
**Earth Alkali Metal Complexes.** Compound **4a** crystallizes in two modifications, the tetragonal modification **4a1** and the monoclinic modification **4a2**. The monoclinic modification was obtained of a hot saturated aqueous



**Figure 3.** Motif A of the structure of  $4a2 \cdot 2.5H_2O$ . Thermal ellipsoids are drawn at the 50% probability level.



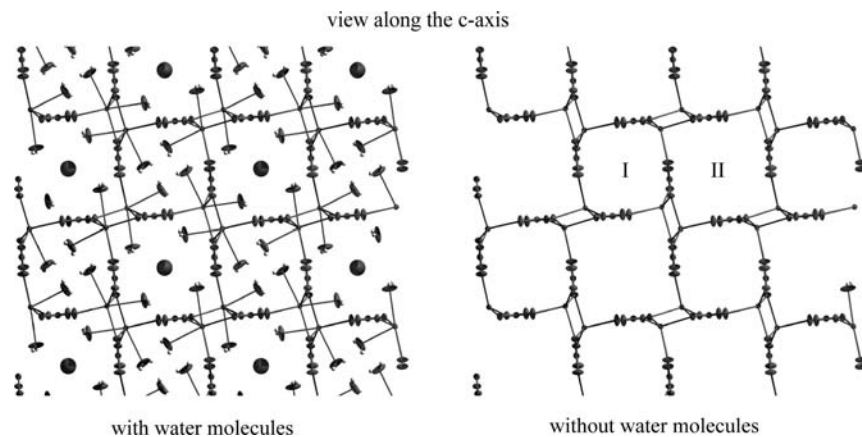
**Figure 4.** Motif B of the structure of  $4a2 \cdot 2.5H_2O$ . Thermal ellipsoids are drawn at the 50% probability level.



**Figure 5.** Motifs A and B of the structure of  $4a1 \cdot 2.75H_2O$ . Thermal ellipsoids are drawn at the 50% probability level.

solution. The more symmetric tetragonal modification was obtained by a slow crystallization at room temperature.

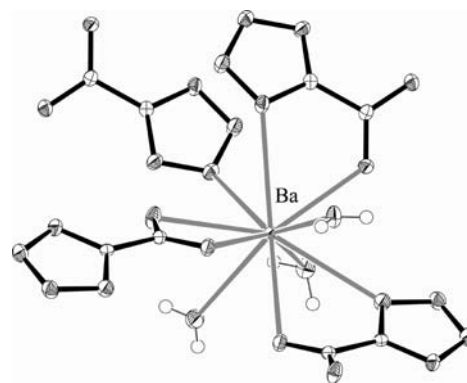
Compound  $4a2 \cdot 2.5H_2O$  crystallizes in the monoclinic space group  $P2(1)c$  with four molecular formulas per unit cell. The asymmetric unit contains four strontium tetrazol-5-carboxylate moieties with 10 molecules of crystal



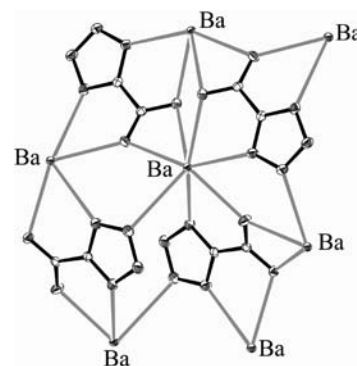
**Figure 6.** View along the *c*-axis of the structure of **4a1**\*2.75H<sub>2</sub>O. Thermal ellipsoids are drawn at the 50% probability level.

water. The structure is built up by two different modes of coordination of the strontium cations. The first structural motif is built up by chains along the *a*-axis, formed by the coordination of the strontium cations to the N2, N3 and O1 and O2 of two different tetrazol-5-carboxylate anions (motif A, Figure 3). In addition, the chains are stabilized by the coordination of the two strontium cations to the bridging water molecules of O42/O43 or O45/O48 (motif A). The second motif contains the connection of two chains by three tetrazol-5-carboxylate moieties (motif B, Figure 4). The coordination of these tetrazol-5-carboxylate anions is similar to the coordination of the copper and manganese salt. One strontium cation is coordinated to O1 and N1, whereas the second cation is coordinated to N2 (motif B). Beside the two main motifs, several tetrazol-5-carboxylate anions are arranged to saturate open positions of coordination, like the tetrazol-5-carboxylate anion 3, coordinated to Sr1 (O31 and N31) and Sr4 (O32). The network of hydrogen bonds stabilizing the structure consists of 19 different hydrogen bonds.

Compound **4a1**\*2.75H<sub>2</sub>O crystallizes in the tetragonal space group *P4/n* with two molecular formulas per unit cell and 2.75 molecules of crystal water per tetrazol-5-carboxylate anion. In contrast to the monoclinic modification the tetragonal modification does only contain two water molecules embedded in the structure. The lesser role of the crystal water compared to **4a2**\*2.5H<sub>2</sub>O is pointed out by the small number of hydrogen bonds formed, compared to **4a2**\*2.5H<sub>2</sub>O (**4a1**\*2.75H<sub>2</sub>O: 5 different hydrogen bonds, **4a2**\*2.5H<sub>2</sub>O: 19 different hydrogen bonds). The structure of **4a1**\*2.75H<sub>2</sub>O is built up by two motifs. Motif A (Figure 5) consists of chains along the *c*-axis. The strontium atom is coordinated to N1 and O1 of two tetrazol-5-carboxylate anions. The connection between the strontium cations is formed by one tetrazol-5-carboxylate anion that is coordinated with its oxygen atom to the first and N2 to the second strontium cation. The remaining free points of coordination are saturated by molecules of water (Figure 5). The chains are connected among each other by hydrogen bonds formed by molecules of water coordinated to the strontium atom (Figure 5). The combination of the chains leads to a porous structure with channels along the *c*-axis (Figure 6). A closer investigation of the channel structure reveals that two different kinds of channels are found as demonstrated in Figure 6. The first channel, channel I, is filled



**Figure 7.** Coordination of the barium atom of **4b**\*3H<sub>2</sub>O. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 8.** Interactions of the tetrazol-5-carboxylate anions with the barium cations of **4b**\*3H<sub>2</sub>O. Thermal ellipsoids are drawn at the 50% probability level.

with the molecules of water attached to the strontium atom. The bigger channel II is filled with strongly distorted molecules of crystal water, which are not involved in the structure, either by coordination to a strontium cation, a tetrazol-5-carboxylate anion, or the formation of hydrogen bonds. Comparing the dimensions of the channels, channel I has a diameter of 7.3 Å, whereas channel II has a diameter of 9.5 Å (measured from one strontium cation to the opposing strontium cation). The crystal water was neglected for the determination of the diameter. If the crystal water attached to the strontium atom is considered for the determination of the diameter,

Table 2. Crystal Structure Solution and Refinement for Tetrazol-5-carboxylate Complexes

	4a1*2.75H <sub>2</sub> O	4a2*2.5H <sub>2</sub> O	4b*3H <sub>2</sub> O	4c*4H <sub>2</sub> O	4d*5H <sub>2</sub> O
formula	C <sub>8</sub> H <sub>16</sub> N <sub>16</sub> O <sub>19</sub> Sr <sub>4</sub>	C <sub>8</sub> H <sub>20</sub> N <sub>16</sub> O <sub>18</sub> Sr <sub>4</sub>	C <sub>2</sub> H <sub>6</sub> Ba <sub>4</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>2</sub> H <sub>8</sub> Cu <sub>4</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>2</sub> H <sub>10</sub> Mn <sub>4</sub> N <sub>4</sub> O <sub>7</sub>
M <sub>r</sub> [g mol <sup>-1</sup> ]	990.85	978.88	303.45	247.65	257.08
crystal system	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P4/n</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> [Å]	12.9854(2)	17.5090(6)	6.6773(2)	15.5106(10)	7.3516(5)
<i>b</i> [Å]	12.9854(2)	9.2732(3)	11.4639(4)	6.4029(4)	12.9931(9)
<i>c</i> [Å]	8.8601(3)	18.4285(7)	10.0846(3)	17.7351(12)	19.8142(16)
α [deg]	90	90	90	90	90
β [deg]	90	106.031(4)	90.856(3)	114.494(8)	100.351(5)
γ [deg]	90	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1494.00	2875.78	771.87	1602.8(2)	1861.85
<i>Z</i>	2	4	4	8	8
<i>F</i> (000)	912.0	1504.0	568.0	1000.0	1048.0
ρ <sub>calc.</sub> [g cm <sup>-3</sup> ]	2.096	1.845	2.611	2.053	1.834
μ [mm <sup>-1</sup> ]	7.19	7.44	5.14	2.74	1.44
2θ [deg]	57.68	53.00	52.99	51.99	49.98
index range	-16 ≤ <i>h</i> ≤ 16 -16 ≤ <i>k</i> ≤ 14 -10 ≤ <i>l</i> ≤ 11	-12 ≤ <i>h</i> ≤ 12 -11 ≤ <i>k</i> ≤ 10 -22 ≤ <i>l</i> ≤ 23	-8 ≤ <i>h</i> ≤ 8 -14 ≤ <i>k</i> ≤ 14 -12 ≤ <i>l</i> ≤ 12	-18 ≤ <i>h</i> ≤ 18 -6 ≤ <i>k</i> ≤ 7 -21 ≤ <i>l</i> ≤ 13	-8 ≤ <i>h</i> ≤ 8 -15 ≤ <i>k</i> ≤ 14 -23 ≤ <i>l</i> ≤ 18
λ	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	200(2)	200(2)	200(2)	200(2)	200(2)
reflections collected	11346	13962	7876	3152	4348
unique reflections	1786	5845	1598	1566	1630
parameter	125	415	133	150	168
<i>S</i>	0.840	0.920	0.981	1.030	0.909
<i>R</i> <sub>int</sub>	0.0349	0.0642	0.0409	0.0257	0.0359
<i>R</i> <sub>1</sub> / w <i>R</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0205/0.0346	0.0463/0.0864	0.0168/0.0387	0.0284/0.0771	0.0276/0.0526
<i>R</i> <sub>1</sub> / w <i>R</i> <sub>2</sub>	0.0426/0.0358	0.1082/0.0984	0.0212/0.0396	0.0369/0.0796	0.0474/0.0561

channel I achieves a diameter of 2.9 Å and channel II 5.1 Å. Taking these results into account, the structure could be able to absorb small atoms or molecules if the distorted, unbound water molecules are removed. This effect could turn this compound into an interesting structure for further investigations in the field of porous materials.

Compound **4b**\*3H<sub>2</sub>O crystallizes in the monoclinic space group *P2(1)c* with four molecular formulas per unit cell and three molecules of crystal water per tetrazol-5-carboxylate. The structure is built up by only one motif, as shown in Figure 7. The barium cation is coordinated to four tetrazol-5-carboxylate anions; two are coordinated by N1 and O1, whereas the third one is coordinated with N2/N3 and the last one with O1 and O2. Each tetrazol-5-carboxylate anion is bound to four barium atoms, two times by N1/N4 and O1/O2 and one time by N2/N3 and O1 and O2 (Figure 8). In addition, the structure is stabilized by six hydrogen bonds between the water molecules and of water molecules to N1 and N2. In contrast to structures **4a1**\*2.75H<sub>2</sub>O and **4a2**\*2.5H<sub>2</sub>O, the barium tetrazol-5-carboxylate forms layers in the *b-c*-plane. Thereby, the barium and tetrazol-5-carboxylate anions are situated in the layer, whereas the crystal water is arranged between these layers. The layers are connected by hydrogen bonds. The shortest distance between two layers neglecting the water molecules is 5.4 Å between the barium cation and N1 of the opposing layer.

The data of the solution and refinement of the crystal structure for the tetrazol-5-carboxylate complexes are given in Table 2. A closer investigation of the bond lengths shows only small differences between the structures. In cases **4c**\*4H<sub>2</sub>O and **4d**\*5H<sub>2</sub>O, the bond length of the coordinated oxygen atom is slightly elongated, compared to the uncoordinated oxygen atom (3.4% in case of **4c**\*4H<sub>2</sub>O and 1.0% in case of **4d**\*5H<sub>2</sub>O).

**Energetic Properties and Flame Color.** The energetic properties were investigated by DSC-measurements, and the sensitivity toward impact and friction was determined by using BAM standards.<sup>24</sup> In case of the determination of the sensitivity against friction, a small sample of the substance is placed on a rough plate made of ceramic and rubbed with a ceramic spike. If the substance shows any decomposition, flame, or detonates at a certain friction force, it is sensitive toward friction up to this value. The sensitivity toward impact is determined by a drop hammer. The substance is placed in a metal sleeve, and a drop hammer of a certain weight is dropped from a certain level. The sensitivity toward impact is defined by the force at which one sample of five shows any decomposition or detonation. The DSC-data were obtained by using the precipitated powder instead of the crystalline solid. The samples were dried under high vacuum to remove any moisture beside crystal water.

The analysis of the thermal stability by DSC-measurements revealed significant differences between the compounds (Figure 9). Comparing the transition metal complexes **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O, the silver tetrazol-5-carboxylate **4e**\*1.56H<sub>2</sub>O was the most thermal unstable compound with a point of decomposition of 200 °C. The decomposition area of **4e**\*1.56H<sub>2</sub>O shows a broad exothermic signal, suggesting a complex mechanism of decomposition. The molecular formula obtained by elemental analysis of **4e**\*1.56H<sub>2</sub>O is (C<sub>14</sub>H<sub>5</sub>N<sub>28</sub>O<sub>14</sub>Ag<sub>9</sub>)\*7H<sub>2</sub>O. In contrast to the other tetrazol-5-carboxylate salts, the DSC-data of **4e**\*1.56H<sub>2</sub>O do not show any clear point of dehydration but a broad area of dehydration ranging from 60 to 140 °C. Compounds **4c**\*3.5H<sub>2</sub>O and **4d**\*4H<sub>2</sub>O possess major differences concerning their thermal behavior, although having both

(24) <http://www.bam.de>.

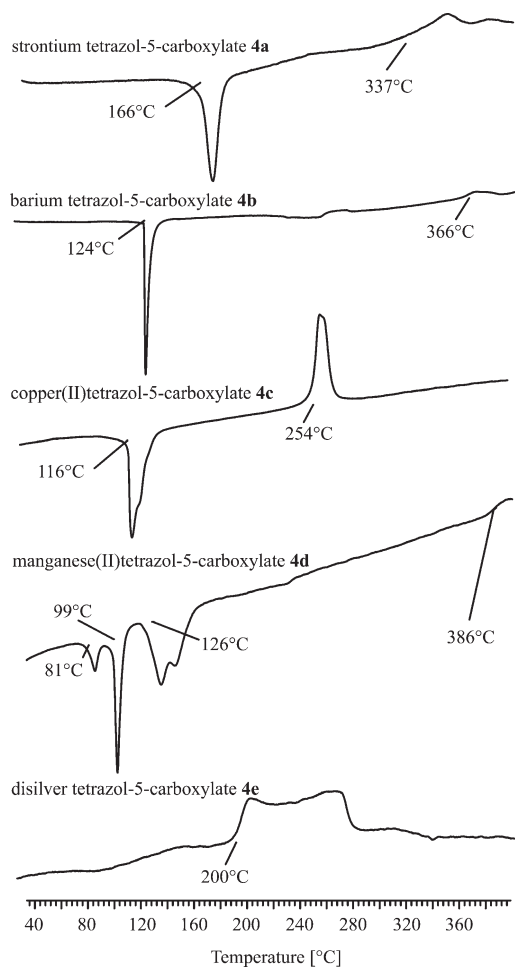


Figure 9. DSC-plots of the tetrazol-5-carboxylate salts.

similar crystal structures. In case of the copper tetrazol-5-carboxylate **4c**\*3.5H<sub>2</sub>O, an endothermic signal at 116 °C indicates the point of dehydration (powder possesses 3.5 molecules of crystal water per copper tetrazol-5-carboxylate). The shoulder of this signal shows that the dehydration takes place in two steps. The point of decomposition at 254 °C is about 130 °C lower than that of the manganese tetrazol-5-carboxylate (386 °C). In contrast to the copper tetrazol-5-carboxylate, the points of dehydration of the manganese tetrazol-5-carboxylate **4d**\*4H<sub>2</sub>O can be clearly distinguished (powder possesses four molecules of crystal water). The first point of dehydration is located at 81 °C, the second at 99 °C, and the third and fourth is merged with an onset of 126 °C.

A comparison between the earth metal salts of tetrazol-5-carboxylate reveals that the thermal stability of the strontium salt **4a**\*3H<sub>2</sub>O is 30 °C lower than that of the barium salt **4b**\*3H<sub>2</sub>O. In contrast to the transition metal tetrazol-5-carboxylates, **4a**\*3H<sub>2</sub>O and **4b**\*3H<sub>2</sub>O possess only one point of dehydration (**4a**\*3H<sub>2</sub>O: 166 °C, **4b**\*3H<sub>2</sub>O: 124 °C). The difference of the points of dehydration of 40 °C proves the weaker bound crystal water in the barium structure **4b**\*3H<sub>2</sub>O. This finding is in accordance with the arrangement of the crystal water in the two structures. In case of the strontium tetrazol-5-carboxylate **4a**\*3H<sub>2</sub>O, the water molecules are involved in the structure and have significant contribution to the stability of the structure. In case of the barium tetrazol-5-carboxylate

**4b**\*3H<sub>2</sub>O, the crystal water is embedded between the barium tetrazol-5-carboxylate layers.

The investigation of the sensitivity of the tetrazol-5-carboxylate salts toward friction and impact points out the higher stability of the tetrazol-5-carboxylate anion, compared to the nitrotetrazolate anion.<sup>16,17</sup> Compounds **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, and **4c**\*1.56H<sub>2</sub>O do not show any sensitivity toward friction and impact. In case of the transition metal salts, the copper tetrazol-5-carboxylate **4c**\*3.5H<sub>2</sub>O possesses a sensitivity toward friction of > 288 N, whereas the manganese tetrazol-5-carboxylate with a sensitivity toward friction of > 324 N is slightly more stable. Both compounds are insensitive toward impact.<sup>24–26</sup> The grain sizes of the sample of **4a**\*3H<sub>2</sub>O and **4b**\*3H<sub>2</sub>O were between 500 and 1000 μm, the grain size of **4c**\*3H<sub>2</sub>O was 80 to 160 μm, and the grain sizes of **4d**\*4H<sub>2</sub>O and **4e**\*1.56H<sub>2</sub>O were between 250 and 500 μm.

The flame color of compounds **4a**\*3H<sub>2</sub>O, **4b**\*3H<sub>2</sub>O, and **4c**\*3.5H<sub>2</sub>O are in accordance with the expected colors. The strontium salt **4a**\*3H<sub>2</sub>O decomposes under emission of a slightly red flame color, whereas the barium salt **4b**\*3H<sub>2</sub>O possesses a pale greenish flame color. In both cases, the intensity of the flame color is not very high because of the stability of the complexes. The intensity of the color could be achieved by higher temperatures of decomposition, using different oxidizers. In case of **4c**\*3.5H<sub>2</sub>O, the flame color is green with a moderate intensity. These findings turn compounds **4a**\*3H<sub>2</sub>O to **4c**\*3.5H<sub>2</sub>O into valuable components for pyrotechnic applications because of their simple high-yield synthesis along with a high thermal stability. Moreover, their insensitivity against friction and impact are another advantage, regarding an industrial application.

## Conclusion

The strontium **4a** (\*3H<sub>2</sub>O, \*2.75H<sub>2</sub>O, \*2.5H<sub>2</sub>O), barium **4b** (\*3H<sub>2</sub>O), copper **4c** (\*3.5H<sub>2</sub>O, \*4H<sub>2</sub>O), manganese **4d** (\*4H<sub>2</sub>O, \*5H<sub>2</sub>O), and silver tetrazol-5-carboxylate **4e** (\*1.56H<sub>2</sub>O) were synthesized and characterized by IR and NMR spectroscopy. In cases of **4a** (\*2.75H<sub>2</sub>O, \*2.5H<sub>2</sub>O), **4b**\*3H<sub>2</sub>O, **4c**\*4H<sub>2</sub>O, and **4d**\*5H<sub>2</sub>O, the crystal structures were determined using single crystal X-ray diffraction. The analysis of the physical and thermal stability of the compounds revealed their insensitivity toward friction and impact, along with thermal stabilities up to 380 °C. The flame coloration of the strontium tetrazol-5-carboxylate **4a**\*3H<sub>2</sub>O (red), barium tetrazol-5-carboxylate **4b**\*3H<sub>2</sub>O (pale greenish), and copper tetrazol-5-carboxylate **4c**\*3.5H<sub>2</sub>O (green) renders these compounds into promising components for pyrotechnic applications. Another advantage of these compounds is their low solubility in water, along with a lack of toxic moieties (nitro groups, azides) or anions (perchlorate). These properties turn the strontium, barium, and copper tetrazol-5-carboxylates into ecologically interesting substitutes for toxic pyrotechnic compositions.

(25) Impact: Insensitive > 40 J, less sensitive = 35 J, sensitive = 4 J, very sensitive = 3 J; friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a. > 80 N, very sensitive = 80 N, extremely sensitive = 10 N. According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates not safe for transport.

(26) T. M. Klapötke, C. M. Rienäcker *Propellants, Explos., Pyrotech.* **2001**, *26*, 43.

The porous structure of the tetragonal modification of the strontium tetrazol-5-carboxylate **4a1**\*2.75H<sub>2</sub>O contains channels along the *c*-axis. The bigger channel with a diameter of 9.5 Å (without crystal water) or 5.1 Å (with crystal water) should be able to absorb small molecules or atoms. This feature could be used for further investigations in the fields of catalysis or purification.

## Experimental Section

**Caution!** Tetrazoles are highly energetic compounds with sensitivity toward heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar gloves and ear plugs) should be used when undertaking work involving these compounds.

**General Procedures.** All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded using a JEOL Eclipse 400 instrument. The spectra were measured in D<sub>2</sub>O. The chemical shifts are given relative to tetramethylsilane (<sup>13</sup>C) or nitromethane (<sup>15</sup>N) as external standards. Infrared (IR) spectra were recorded using a Perkin–Elmer Spectrum One FT-IR instrument and KBr pellets at room temperature. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Points of dehydration and decomposition were determined using differential scanning calorimetry (Linseis DSC PT-10 instrument. Measurements were performed at a heating rate of 5 °C min<sup>-1</sup> in closed aluminum containers with a hole (1 μm) on the top for gas release with a nitrogen flow of 5 mL min<sup>-1</sup>. The reference sample was a closed aluminum container. The sensitivity data were performed using a BAM drophammer and a BAM friction tester. The calculations of vibrational spectra of **13** were obtained using DFT BLYP/6-31G\* after optimizing the geometry using the Gaussian 03 software<sup>15</sup>. The crystallographic data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved using direct methods (SHELXS-97)<sup>27</sup> and refined using SHELXL-97<sup>28</sup>. All non-hydrogen atoms were refined anisotropically. Oak Ridge Thermal Ellipsoid Plots (ORTEPs) show the thermal ellipsoids with 50% probability for the non-hydrogen atoms.

The dipotassium and disodium tetrazol-5-carboxylate was synthesized after a European patent.<sup>29</sup>

**General Synthesis for Metal Tetrazol-5-carboxylates.** Crude dipotassium tetrazol-5-carboxylate (1.0 g, 5.3 mmol) was dissolved in 6 mL of 2 N nitric acid to remove residues of potassium carbonate. A saturated solution of the corresponding metal nitrate (15.9 mmol) was added at room temperature under vigorous stirring.

In case of **4c**\*3.5H<sub>2</sub>O, **4d**\*4H<sub>2</sub>O, and **4e**\*1.56H<sub>2</sub>O, the product instantly precipitated as turquoise (**4c**\*3.5H<sub>2</sub>O) or colorless (**4d**\*4H<sub>2</sub>O and **4e**\*1.56H<sub>2</sub>O) powder. The solvent was removed by filtration, and the solid was washed with 50 mL of water and 20 mL of methanol. The product was dried under high vacuum.

In case of **4a**\*3H<sub>2</sub>O and **4b**\*3H<sub>2</sub>O, the resulting solution was kept at room temperature, and the product was obtained by slow crystallization. The formed crystals were collected by filtration and were washed with 50 mL of water and 20 mL of methanol. The product was dried under high vacuum.

**Strontium Tetrazol-5-carboxylate 4a\*3H<sub>2</sub>O.** Yield: 68%; dehydr. 166 °C, dec 337 °C; IR (KBr) (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3429 (vs), 2964 (w), 2920 (vw), 2853 (vw), 2802 (vw), 2708 (vw), 2639 (vw), 2613 (vw), 2449 (vw), 2419 (vw), 1987 (vw), 1789 (w), 1678 (m), 1622 (vs), 1487 (m), 1437 (m), 1414 (m), 1372 (s), 1326 (s), 1309 (m), 1262 (m), 1230 (w), 1217 (w), 1188 (w), 1110 (w), 1093 (w), 1067 (w), 1054 (w), 1014 (w), 949 (vw), 839 (vw), 814 (m), 736 (w), 711 (w), 683 (w), 658 (w), 575 (w), 547 (w), 464 (w); elemental analysis calcd (%) for Sr<sub>2</sub>(C<sub>6</sub>N<sub>12</sub>O<sub>6</sub>)\*6H<sub>2</sub>O (621.89): C 11.60, H 2.27, N 27.04; found: C 11.60, H 2.44, N 27.31.

**Barium Tetrazol-5-carboxylate 4b\*3H<sub>2</sub>O.** Yield: 70%; dehydr. 124 °C, dec 366 °C; IR (KBr) (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3541 (vs), 3458 (vs), 3377 (vs), 3229 (vs), 2547 (vw), 2457 (vw), 2289 (vw), 2213 (vw), 2196 (vw), 2182 (vw), 2120 (vw), 2106 (vw), 2091 (vw), 2075 (vw), 1945 (vw), 1857 (vw), 1667 (m), 1576 (vs), 1490 (vs), 1389 (vs), 1323 (vs), 1182 (s), 1149 (m), 1067 (w), 1054 (m), 1037 (m), 830 (vs), 770 (m), 732 (m), 703 (m), 674 (m), 543 (m), 523 (m), 454 (w); elemental analysis calcd (%) for Ba(C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>)\*3H<sub>2</sub>O: C 7.92, H 1.99, N 18.47; found: C 7.99, H 1.99, N 18.55.

**Copper(II)tetrazol-5-carboxylate 4c\*3.5H<sub>2</sub>O.** Yield: 91%; dehydr. 116 °C, dec 254 °C; IR (KBr) (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3426 (vs), 3098 (m), 2501 (vw), 2324 (vw), 2214 (vw), 1661 (m), 1630 (m), 1487 (m), 1430 (m), 1382 (w), 1320 (m), 1262 (w), 1231 (w), 1192 (w), 1136 (w), 1083 (w), 1055 (vw), 834 (w), 817 (w), 670 (w), 627 (w), 578 (w); elemental analysis calcd (%) for Cu(C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>)\*3.5H<sub>2</sub>O: C 10.07, H 2.96, N 23.48; found: C 10.03, H 2.82, N 23.45.

**Manganese(II)tetrazol-5-carboxylate 4d\*4H<sub>2</sub>O.** Yield: 85%; dehydr. 81 °C, 99 °C, 126 °C, dec 386 °C; IR (KBr) (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3440 (vs), 3381 (vs), 3289 (vs), 3177 (s), 2289 (vw), 2218 (vw), 1652 (vs), 1635 (vs), 1484 (m), 1409 (m), 1382 (w), 1323 (s), 1262 (w), 1217 (w), 1179 (w), 1115 (w), 1083 (w), 1064 (w), 834 (m), 825 (w), 679 (m), 478 (w); elemental analysis calcd (%) for Mn(C<sub>2</sub>N<sub>4</sub>O<sub>2</sub>)\*4H<sub>2</sub>O: C 9.34, H 3.92, N 21.80; found: C 9.20, H 3.68, N 21.69.

**Disilver tetrazol-5-carboxylate 4e\*1.56H<sub>2</sub>O.** Yield: 98%; dec 200 °C; IR (KBr) (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3431 (m), 2962 (vw), 2924 (vw), 2101 (vw), 1615 (vs), 1468 (m), 1382 (m), 1323 (m), 1261 (w), 1175 (w), 1140 (w), 1099 (w), 1055 (w), 1037 (w), 875 (w), 833 (w), 811 (m), 693 (w), 670 (w), 576 (w); elemental analysis calcd (%) for (Ag<sub>9</sub>C<sub>14</sub>H<sub>5</sub>N<sub>28</sub>O<sub>14</sub>)\*7H<sub>2</sub>O: C 8.91, H 1.02, N 20.79; found: C 8.76, H 0.92, N 20.86.

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**Supporting Information Available:** Crystallographic data in CIF file format. This material is available free of charge via the Internet at <http://pubs.acs.org>. Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)) on quoting the depository number CSD-420720(**4a1**\*2.75H<sub>2</sub>O), 420719 (**4a2**\*2.5H<sub>2</sub>O), 420716 (**4b**\*3H<sub>2</sub>O), 420717 (**4c**\*4H<sub>2</sub>O) and 420718 (**4d**\*5H<sub>2</sub>O).

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