

Pyrotechnically Relevant Salts of 1-(2-Chloroethyl)-5-nitriminotetrazole – Synthesis and Coloring Properties

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Abstract: Alkaline and alkaline earth metal salts are widely used in pyrotechnic formulations as colorant agents. Salts of strontium are responsible for a red flame color, barium salts, mostly $Ba(NO_3)_2$, for a green one and copper salts, only combined with a chlorine donor, are able to yield a blue flame color. To investigate the possibility of reducing the amount of metal in pyrotechnic formulations producing colored flames, the strontium and barium salts of 1-(2-chloroethyl)-5-nitriminotetrazole, *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato- $\kappa^2 N^4, O^5$ }copper(II)] dihydrate, copper(II) 1-(2-chloroethyl)-5-nitriminotetrazolate and *trans*-[diammine-bis{1-(2-chloroethyl)-5-nitriminotetrazolate- $\kappa^2 N^4, O^1$ }copper(II)] were synthesized and characterized using IR and Raman spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). Their sensitivities towards shock, friction, and electric discharge and the solubility in H_2O at ambient temperature were determined. Heats of formation were calculated using bomb calorimetric measurements. Crystal structures of all compounds have been determined by single crystal X-ray diffraction and a detailed description is given. Last but not least, all salts were tested with regard to their color performance.

Keywords: pyrotechnics, coloring agent, tetrazoles, perchlorate-free.

Introduction

Nitrogen-rich compounds and in particular their metal salts and copper(II) compounds play a key role in the development of environmentally benign pyrotechnics.¹⁻³ Smokeless combustion, caused by the formation of mainly gaseous products, is one reason nitrogen-rich substances seem to be a good alternative. Furthermore, this class of substances gains its energy from high heats of formation rather than from the oxidation of a carbon backbone or a fuel. Even more promising seem to be tetrazoles, which exhibit energetic nitrogen-oxygen containing functional groups such as nitro groups ($R-NO_2$),^{4,5} nitrate esters ($R-O-NO_2$)⁶ or nitramine functionalities (R_2N-NO_2),⁷⁻⁹ since these compounds have balanced oxygen contents.

5-Nitriminotetrazoles have been known for a long

time, since they are obtainable via facile synthetic routes.¹⁰ 1-Substituted 5-nitriminotetrazoles, e.g. 1-methyl-5-nitriminotetrazole and 1-ethyl-5-nitriminotetrazole, were first described in 1957.¹¹ Another advantage of these substances is that they can be deprotonated yielding thermally stable anions or serve as ligands in several metal complexes.¹²

Colors in pyrotechnics are obtained by the addition of chemicals that produce substances that combine in the flame and emit the desired radiation. Emission of green light is achieved by the addition of barium nitrate, which acts as both coloring agent and oxidizer. This is true for strontium nitrate, the agent for intensive red colors. The corresponding light emitting species (in the gas phase) are the monohydroxides, SrOH and BaOH, and the monochlorides, SrCl and BaCl,

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respectively. If a blue flame is desired, usually copper or copper compounds are combined with a chlorine donor like PVC (poly vinyl chloride). This is necessary, since the formation of CuCl is responsible for the emitting of blue light.¹³ If no chlorine is present or the temperature rises above 1200 °C in an oxygen-rich flame, CuOH and CuO – light emitting species of green and red, respectively – are formed.¹⁴ Chlorine containing species like potassium perchlorate are widely added to common fireworks for red, green or blue flame colors on this account, besides its property as an oxidizer.

Recently, several strontium salts of different 5-nitriminotetrazoles and their properties as coloring agents to find application in pyrotechnic compositions were presented.¹⁵ The same is true for different barium tetrazole derivatives.¹⁶

Pyrotechnic applications and fireworks cause manifold environmental pollution, as shown in several studies.¹ One main pollutant is perchlorate which is added as an oxidizer in most pyrotechnic compositions. It is a high energy oxidizer with good thermal and chemical stability. However, the presence of potassium perchlorate, like all perchlorates, in drinking water is a cause of concern, because of their known ingestion to inhibit iodide uptake by the thyroid gland. Therefore, in our research group concentrated efforts are spent on the substitution of perchlorate in pyrotechnic compositions. An alternative is presented in a recently published paper.² Another study in which potassium perchlorate is replaced by potassium, sodium or strontium nitrate is known in the literature.¹⁷ In the cases where these salts are used

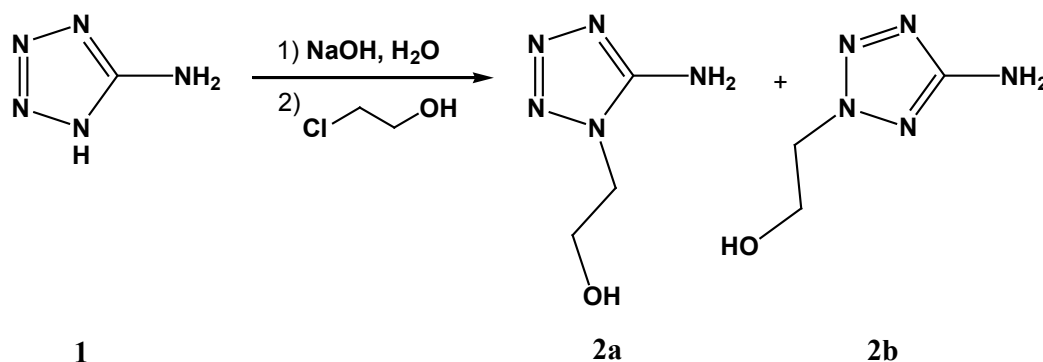
as oxidizers, there is a lack of a chlorine donor, which guarantees a more intense flame color, especially in the combination with strontium (red), barium (green) or copper (blue) salts. Therefore, the strontium and barium salts of 1-(2-chloroethyl)-5-nitriminotetrazole, *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato- κ^2N^4, O^5 }copper(II)] dihydrate, copper(II) 1-(2-chloroethyl)-5-nitriminotetrazolate and *trans*-[diammine-bis{1-(2-chloroethyl)-5-nitriminotetrazolato- κ^2N^4, O^1 }copper(II)] were prepared. In addition to the syntheses a comprehensive characterization of the chemical as well as the energetic properties is given. Furthermore, all compounds were tested with regard to their color performance and some pyrotechnic compositions are presented in this work.

Results and discussion

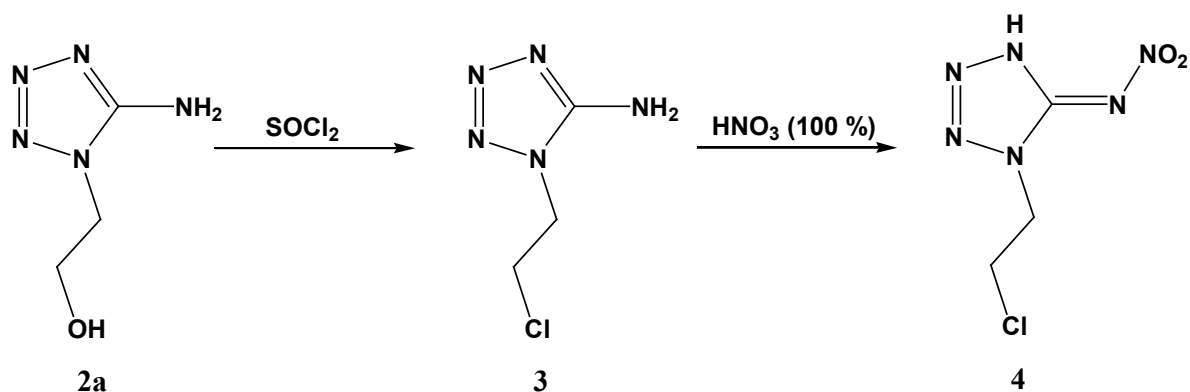
Syntheses

The alkylation of 5-amino-1*H*-tetrazole (**1**) with 2-chloroethanol was performed according to the literature (Scheme 1).^{18,19} Both isomers 1- and 2-(2-hydroxyethyl)-5-aminotetrazole could be isolated. Since the work up of the 2-isomer (**2b**) is extremely time-consuming, further reaction steps were only realized with 1-(2-hydroxyethyl)-5-aminotetrazole (**2a**).

1-(2-Chloroethyl)-5-aminotetrazole (**3**) could be obtained *via* chlorination of **2a** with thionyl chloride according to Finnegan and Henry (Scheme 2).²⁰ The nitration of **3** was performed in HNO₃ (100%), which procedure is well known in the literature.^{7,19} Therefore, compound **3** was slowly added to an ice-cooled solution of HNO₃



Scheme 1. Preparation of 1- and 2-(2-hydroxyethyl)-5-aminotetrazole (**2a**, **b**), starting from 5-amino-1*H*-tetrazole (**1**).



Scheme 2. Preparation of 1-(2-chloroethyl)-5-aminotetrazole (3) and 1-(2-chloroethyl)-5-nitriminotetrazole (4).

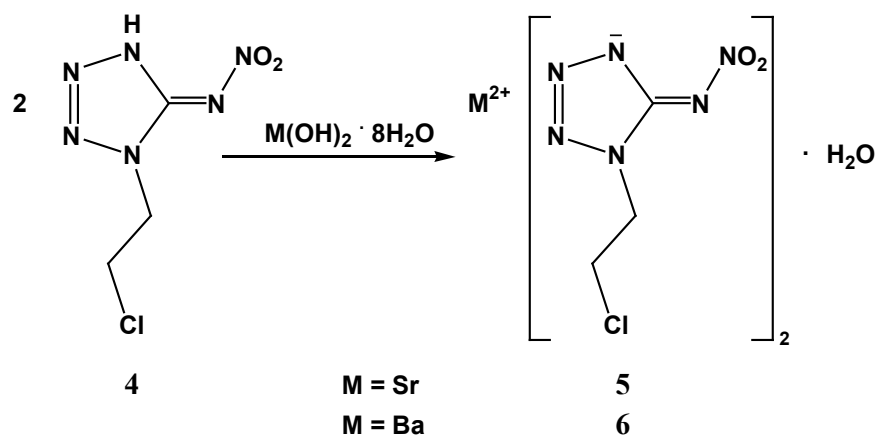
(100%) and stirred for at least 17 hours. Afterwards the colorless solution was poured on to ice. After recrystallization from H_2O 1-(2-chloroethyl)-5-nitriminotetrazole (4) could be obtained in a yield of 93%.

For preparation of strontium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (5) and barium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (6) compound 4 was reacted with the corresponding hydroxides in H_2O (Scheme 3). Both salts 5 and 6 could be obtained in very good yields of 91% and 95%, respectively.

The copper(II) complex diaqua *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato- κ^2N^4, O^5 }copper(II)] dihydrate (7) is described in the

literature.¹⁹ It could be obtained by the reaction with either copper(II) chloride dihydrate or copper(II) nitrate pentahemihydrate (Scheme 4). The water free copper salt copper(II) 1-(2-chloroethyl)-5-nitriminotetrazolate (8) was prepared by removing the coordinated water of powdered 7 at 110 °C in almost quantitative yields.

In the presence of diluted ammonia solution *trans*-[diammine-bis{1-(2-chloroethyl)-5-nitriminotetrazolato- κ^2N^4, O^1 }copper(II) (9) was obtained from 4 and the copper(II) nitrate solution. Deep violet crystals formed after storing the solution for a few days at ambient temperature.



Scheme 3. Synthesis of strontium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (5) and barium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (6).

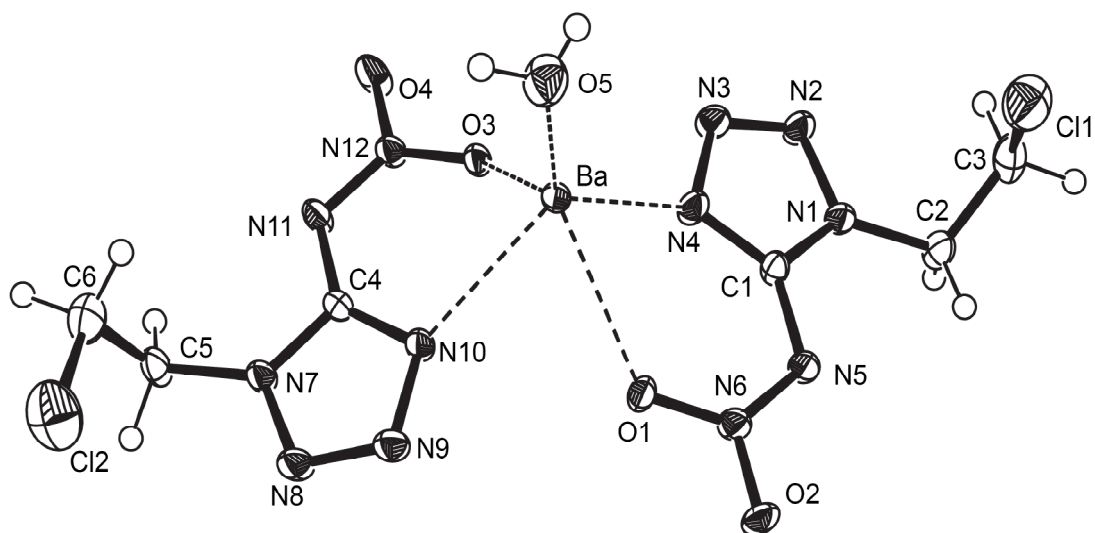


Figure 2. Molecular unit of **6**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability. Selected geometries: distances (Å) N1–N2 1.353(5), N7–N8 1.348(5), N2–N3 1.287(5), N8–N9 1.292(5), N3–N4 1.369(5), N9–N10 1.373(5), N5–N6 1.296(5), N11–N12 1.306(5), N4–C1 1.331(5), N10–C4 1.320(5), N1–C1 1.350(5), N7–C4 1.349(5), N5–C1 1.381(5), N11–C4 1.382(5), O1–N6 1.273(4), O3–N12 1.266(4), O2–N6 1.268(4), O4–N12 1.258(4), Ba–N4 2.908(4), Ba–N10 2.944(3), Ba–O1 2.864(3), Ba–O3 2.841(3), Ba–O5 2.767(4), N1–C2 1.463(5), N7–C5 1.463(5), C2–C3 1.514(6), C5–C6 1.510(7), Cl1–C3 1.783(5), Cl2–C6 1.794(6); angles (°) N6–N5–C1 116.7(3), N12–N11–C4 116.2(3), O1–N6–N5 125.0(3), O3–N12–N11 124.8(3), O2–N6–O1 117.9(3), O4–N12–O3 118.5(3), N4–Ba–O1 129.68(9), N10–Ba–O3 128.13(8); torsion angles (°) N6–N5–C1–N4 8.9(7), C1–N5–N6–O1 –0.2(6).

6 and **9** were solved with SIR-92,²³ **8** with SIR-97²⁴ and refined with SHELXL-97²⁵ and finally checked using the PLATON software.²⁶ The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by the SCALE3 ABSPACK multi-scan method.²⁷ All relevant data and parameters of the X-ray measurements and refinements are given in Table 1. Further information on the crystal-structure determinations has been deposited with the Cambridge Crystallographic Data Centre (CCDC)²⁸ as supplementary publications 718890 (**5**), 718891 (**6**) 733993 (**8**) and 733994 (**9**). The structure of **7** (CCDC 704305) is discussed in Klapötke *et al.*¹⁹

The strontium salt **5** crystallizes with one molecule of water of crystallization in the orthorhombic space group *Pbca*. One unit cell contains eight formula units (Figure 1). The calculated density is 2.033 g cm⁻³. The strontium cation is coordinated by the atoms O1, O2, O3, O4, N3, N4, N9, N10 and the oxygen atom of the

crystal water (O5). The oxygen atoms O1 and O3 are each coordinated to two different strontium atoms. Three different hydrogen bonds can be observed. In each case O5 is the donor atom (H⋯A (Å): H1a⋯N2ⁱ 2.40(6), H1a⋯O2ⁱⁱ 2.51(7), H1b⋯N5ⁱⁱ 2.49(4); D⋯A (Å): O5⋯N2ⁱ 3.233(7), O5⋯O2ⁱⁱ 2.936(6), O5⋯N5ⁱⁱ 3.250(7); angle DHA (°): O5H1aN2ⁱ 173(8), O5H1aO2ⁱⁱ 113(6), O5H1bN5ⁱⁱ 151(8); *i*: $x + 1/2, -y + 1/2, -z + 1$, *ii*: $x + 1/2, -y + 3/2, -z + 1$). The nitrimino group of both anions follows the planarity of the tetrazole ring with a twist angle of ~0° (C1–N5–N6–O1) and ~1° (C4–N11–N12–O3), respectively.

By analogy with strontium 1-methyl-5-nitrimino-tetrazolate monohydrate¹⁵ the packing of **5** is strongly influenced by the formation of stacks. The crystal water molecules effect no bridging and are coordinated alternately up and down.

The barium salt **6** crystallizes in the monoclinic space group *P21* with only two formula units per unit cell (Figure 2). Its density of 2.180 g cm⁻³ is comparable to that of **5**. The atoms coordinated to the barium atoms are analogous to those of the

Table 1. Crystallographic data of 5, 6, 8 and 9.

	5	6	8	9
Formula	C ₆ H ₁₀ Cl ₂ N ₁₂ O ₅ Sr	C ₆ H ₁₀ BaCl ₂ N ₁₂ O ₅	C ₆ H ₈ Cl ₂ CuN ₁₂ O ₄	C ₆ H ₁₄ Cl ₂ CuN ₁₄ O ₄
<i>M</i> [g mol ⁻¹]	488.78	538.50	446.68	480.75
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	<i>Pbca</i> (61)	<i>P</i> $\bar{1}$ (2)	<i>P2</i> ₁ / <i>c</i> (14)	<i>P2</i> ₁ / <i>c</i> (14)
Color/habit	colorless blocks	colorless plates	green disks	blue pads
Size [mm]	0.12 × 0.11 × 0.07	0.10 × 0.10 × 0.03	0.32 × 0.25 × 0.03	0.4 × 0.2 × 0.01
<i>a</i> [Å]	12.9331(4)	8.5674(2)	11.273(6)	14.4769(5)
<i>b</i> [Å]	8.3175(3)	9.0807(3)	6.451(3)	5.5805(2)
<i>c</i> [Å]	29.6896(10)	11.8239(3)	9.685(5)	10.7259(5)
α [°]	90	98.756(3)	90	90
β [°]	90	96.802(2)	90.925(5)	101.154(4)
γ [°]	90	113.050(3)	90	90
<i>V</i> [Å ³]	3193.74(19)	820.38(5)	704.2(7)	850.16(6)
<i>Z</i>	8	2	2	2
ρ_{calc} [g cm ⁻³]	2.033	2.180	2.107	1.878
μ [mm ⁻¹]	3.765	2.798	1.981	1.651
<i>F</i> (000)	1936	520	446	486
$\mu\text{MoK}\alpha$ [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	200	200	100	200
θ min–max [°]	3.99, 26.0	3.88, 26.0	3.79, 28.7	3.86, 26.0
Dataset [<i>h</i> , <i>k</i> , <i>l</i>]	–10:15; –9:10; –36:36	–10:10; –11:11; –14:14	–13:13; –7:7; –11:11	–17:11; –3:6; –13:11
Reflections collected	15296	18013	4557	3194
Independent reflections	3120	3205	1371	1661
<i>R</i> _{int}	0.0756	0.0327	0.0345	0.0237
Observed reflections	1862	2849	1138	1284
No. parameters	243	243	115	136
Restraints	3	0	0	0
<i>R</i> ₁ (obs)	0.0428	0.0265	0.0409	0.0254
<i>wR</i> ₂ (all data)	0.1358	0.0691	0.1285	0.0573
GooF	1.047	1.118	1.142	0.922
Resd. dens. [<i>e</i> Å ⁻³]	–1.242, 1.635	–0.734, 1.392	–1.014, 0.710	–0.244, 0.353
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	718890	718891	733993	733994

strontium atoms in **5**. Furthermore, the nitrimino group is not twisted out of the tetrazole ring plane. One hydrogen bond with the parameters ($H\cdots A$ (Å): $H1b\cdots O2^i$ 2.047; DHA (°): 166.98; $D\cdots A$ (Å): $O5\cdots O2^i$ 2.858; $i: x, y - 1, z$) can be found. Both **5** and **6** show similar bond lengths and angles of their anions.

The packing of **6** is also dominated by stacks, formed along the a axis with the crystal water molecules coordinated alternately up and down.

The copper salt **8** crystallizes analogously to *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitrimino-tetrazolato- $\kappa^2 N^4, O^5$ }copper(II)] dihydrate (**7**) in the monoclinic space group $P2_1/c$ with two molecular units per unit cell.¹⁹ As expected, the calculated density of **8** (2.107 g cm⁻³) is higher than that of **7** (1.871 g cm⁻³).¹⁹ The copper(II) atoms are located on the center of inversion, whereby the 1-(2-chloroethyl)-5-nitriminotetrazole anions act as bidentate ligands (Figure 3). A Jahn–Teller-distorted octahedral coordination of the copper cations is observed. Interestingly, the Cu–N4 and Cu–O1 distances are equal to 1.954 Å and the distance between the copper cation and O2 of 2.602 Å is the longest. No hydrogen bonds could be observed.

Copper(II) complex **9** also crystallizes in the space group $P2_1/c$ with two molecular units per unit cell (Figure 4). The calculated density of 1.878 g cm⁻³ is comparable with that of **7**. Analogous to **8**, the copper(II) cations are located on the center of inversion and are coordinated by the 5-nitriminotetrazole anions and neutral ammonia ligands forming a Jahn–Teller-distorted octahedron. The copper nitrogen distances are comparable in length (Cu–N4 2.011(2) Å and Cu–N7 2.005(2) Å), but the Cu–O1 distance is clearly longer at 2.352(2) Å, which is in agreement with the coordination sphere in **7**.

Energetic properties

The energetic properties, such as decomposition temperature (T_{dec}), sensitivity towards shock (E_{dt}), friction (F_r) and electric discharge (E_{el}), and combustion energy ($\Delta_c U$), were determined or adopted from the literature. Furthermore, the solubility in H₂O at ambient temperature of each compound was defined. An overview of the energetic properties of **5–9** is given in Table 2.

The thermal behavior of *ca.* 2 mg of the compounds **5–9** was determined *via* differential scanning calorimetry (DSC) in the temperature range

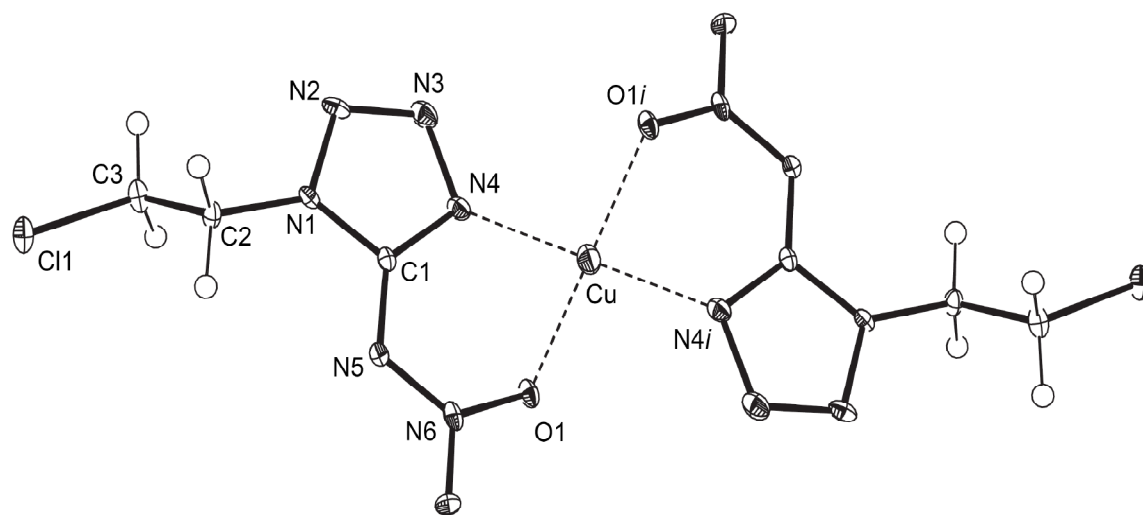


Figure 3. Molecular unit of **8**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability. Selected geometries: distances (Å) N1–N2 1.362(4), N2–N3 1.280(5), N3–N4 1.381(5), N5–N6 1.308(5), N4–C1 1.329(5), N1–C1 1.347(5), N5–C1 1.362(5), O1–N6 1.293(4), O2–N6 1.245(4), Cu–N4 1.954(3), Cu–O1 1.954(3), N1–C2 1.463(5), C2–C3 1.515(5), Cl1–C3 1.785(4); angles (°) N6–N5–C1 117.1(3), O1–N6–N5 124.8(3), O2–N6–O1 117.9(3), N4–Cu–O1 84.81(13); torsion angles (°) N6–N5–C1–N4 –10.6(6), C1–N5–N6–O1 –3.4(5).

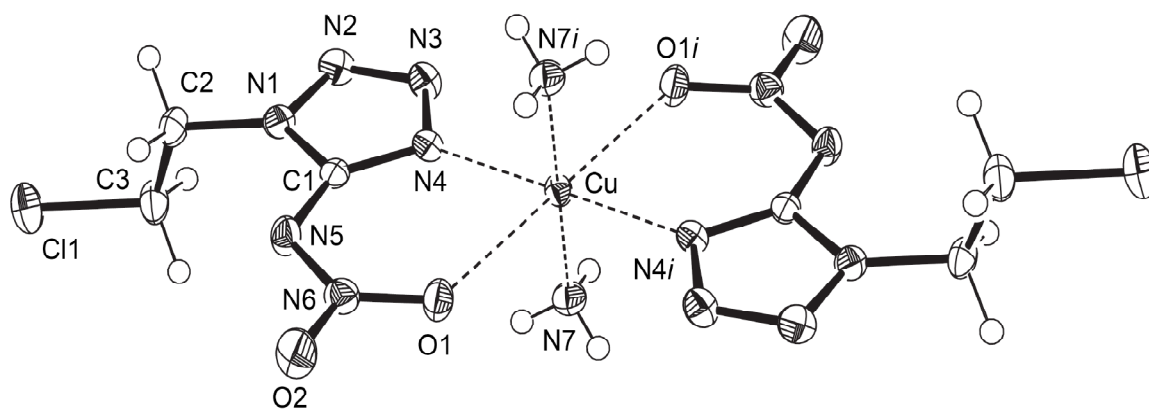


Figure 4. Molecular unit of **9**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability. Selected geometries: distances (Å) N1–N2 1.343(2), N2–N3 1.286(2), N3–N4 1.362(2), N5–N6 1.318(2), N4–C1 1.332(3), N1–C1 1.356(2), N5–C1 1.359(3), O1–N6 1.262(2), O2–N6 1.241(2), Cu–N4 2.011(2), Cu–O1 2.352(2), Cu–N7 2.005(2), N1–C2 1.456(2), C2–C3 1.509(3), C11–C3 1.788(2); angles (°) N6–N5–C1 117.3(2), O1–N6–N5 123.6(2), O2–N6–O1 118.8(2), N4–Cu–O1 76.04(6), N4–Cu–N7 88.81(9) N7–Cu–O1 90.05(8); torsion angles (°) N6–N5–C1–N4 –8.4(4), C1–N5–N6–O1 –2.4(3).

from 50 °C to 400 °C. All prepared substances decompose above 200 °C, whereby the copper(II) compounds **7** and **8** offer the highest decomposition temperatures of 242 °C and 238 °C, respectively. In

view of this fact and that **7** loses H₂O at 103 °C, it was possible to obtain **8** by removing the chemical water of **7**. In the case of copper(II) complex **9** no loss of ammonia could be observed.

Table 2. Overview of the physico-chemical properties of **5–9**.

	5	6	7	8	9
Formula	C ₆ H ₁₀ Cl ₂ N ₁₂ O ₅ Sr	C ₆ H ₁₀ BaCl ₂ N ₁₂ O ₅	C ₆ H ₁₆ Cl ₂ CuN ₁₂ O ₈	C ₆ H ₈ Cl ₂ CuN ₁₂ O ₄	C ₆ H ₁₄ Cl ₂ CuN ₁₄ O ₄
<i>M</i> [g mol ⁻¹]	488.78	538.50	518.72	446.68	480.75
<i>E</i> _{dr} [J] ^a	10	3.0	>50	6.0	6.0
<i>F</i> _r [N] ^b	>360	144	>360	192	>360
<i>E</i> _{cl} [J] ^c	0.75	1.0	0.60	0.50	0.50
<i>N</i> [%] ^d	34.4	31.2	32.4	37.6	40.8
<i>Ω</i> [%] ^e	-39	-36	-37	-43	-53
<i>T</i> _{dec} [°C] ^f	208	207	242	238	205
<i>ρ</i> [g cm ⁻³] ^g	2.03	2.18	1.87 ¹⁹	2.11	1.89
<i>Δ</i> _c <i>U</i> [kJ kg ⁻¹] ^h	-7030	-6330	-7042	-8797	-10238
<i>Δ</i> _c <i>H</i> ^o [kJ mol ⁻¹] ⁱ	-3416	-3389	-3633	-3908	-4893
<i>Δ</i> _f <i>H</i> ^o [kJ mol ⁻¹] ^j	-863	-846	-1068	346	474
<i>Δ</i> _f <i>U</i> [kJ kg ⁻¹] ^k	-1691	-1504	-1969	775	987
H ₂ O sol. [wt%] ^l	14 (21 °C)	0.8 (21 °C)	0.9 (23 °C)	0.7 (23 °C)	0.4 (23 °C)

^a BAM drop hammer. ^b BAM methods. ^c Electric spark tester. ^d Nitrogen content. ^e Oxygen balance. ^f Decomposition temperature from DSC ($\beta = 5 \text{ °C min}^{-1}$). ^g Determined by X-ray crystallography. ^h Combustion energy. ⁱ Enthalpy of combustion. ^j Molar enthalpy of formation. ^k Energy of formation. ^l Solubility in H₂O (H₂O temperature).

The compounds **5**, **6**, **8**, and **9** are sensitive to shock according to the literature.²⁹ Salt **5** shows the lowest sensitivity (10 J), but it is insensitive towards friction. The barium salt **6** is very sensitive towards shock (3.0 J) and sensitive towards friction (144 N). The copper(II) complexes **7** and **9** are insensitive towards friction. Salt **7** is also insensitive towards shock, whereas **9** offers a impact sensitivity of 6.0 J and the water free compound **8** is sensitive towards both stimuli (E_{dr} : 6 J, F_r : 192 N). This is a verification that the inclusion of crystal water decreases the sensitivity.

All determined values for the electrostatic sensitivity are in the range of 0.5–1.0 J (**8**, **9**: 0.50 J; **7**: 0.60 J; **5**: 0.75 J; **6**: 1.0 J). These results are consistent with the sensitivities of other insensitive energetic materials.

The reported values of the combustion energy ($\Delta_c U$) are the average of three single bomb calorimetry measurements. The standard molar enthalpy of combustion ($\Delta_c H^\circ$) was derived from equation (1).

$$\Delta_c H^\circ = \Delta_c U + \Delta n RT \quad (1)$$

$$\Delta n = \sum n_i (\text{gaseous products}) - \sum n_i (\text{gaseous starting materials})$$

n_i = molar amount of gas i .

The enthalpy of formation ($\Delta_f H^\circ$) for each compound **5–9** was calculated at 298.15 K using the Hess thermochemical cycle and the following combustion reactions (Scheme 5). The heats of formation of the combustion products $\text{H}_2\text{O}_{(l)}$ (-286 kJ mol^{-1}), $\text{CO}_{2(g)}$ (-393 kJ mol^{-1}), $\text{HCl}_{(g)}$ ($-92.3 \text{ kJ mol}^{-1}$), $\text{SrO}_{(s)}$ (-592 kJ mol^{-1}), $\text{BaO}_{(s)}$ (-548 kJ mol^{-1}), and $\text{CuO}_{(s)}$ (-157 kJ mol^{-1}) were

adopted from the literature.³⁰

Except for **8** and **9** all compounds were calculated to be formed exothermically. Copper complex **7** shows the highest negative value for the heat of formation ($-1068 \text{ kJ mol}^{-1}$). In contrast to that, the copper compounds **8** and **9** offer the highest positive ones. The calculated values of **5** and **6** are comparable.

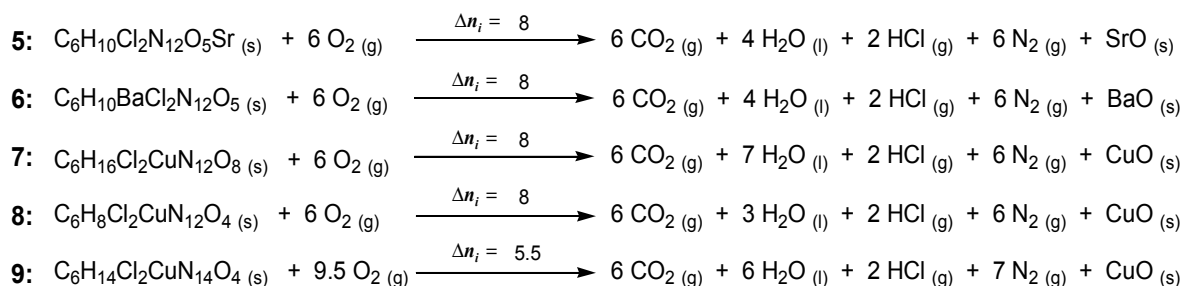
For determining the solubility of **5–9**, each compound was added to 1 mL H_2O at the noted temperature until the solution was saturated. The solubilities of **5–9** are given in weight percent (wt%) and were calculated according to equation (2).

$$\text{wt}\% = \frac{m_{\text{dissolvedCompound}}}{m_{\text{dissolvedCompound}} + m_{\text{Solvent}}} \cdot 100 \quad (2)$$

The strontium salt **5** offers the highest solubility with 14 wt%. All other compounds **6–9** are almost insoluble in H_2O under these conditions with solubilities below 1.0 wt%.

Coloring properties and some pyrotechnic compositions

All compounds **5–9** show the expected flame color – with regard to their corresponding cations – in the flame of a Bunsen burner (Figure 5). Furthermore, their combustion occurs without smoke production. The strontium salt **5** combusts with a very intense red flame, significantly more intense than the other nitrogen-rich salts strontium 5-nitriminotetrazolate dihydrate, strontium (5-nitrimino-1*H*-tetrazolate) tetrahydrate,



Scheme 5. Combustion equations of **5–9**.



Figure 5. Color performance of (top to bottom) 5–9 in the flame of a Bunsen burner.

strontium (1-methyl-5-nitriminotetrazolate) monohydrate and strontium (2-methyl-5-nitriminotetrazolate).¹⁵ A very intense green flame is shown by 6, also significantly more intense than other barium salts like barium tetrazolate,

barium 5-aminotetrazolate tetrahydrate, barium 5-nitriminotetrazolate dihydrate, barium bis(5-nitrimino-1*H*-tetrazolate) tetrahydrate, barium 1-methyl-5-nitriminotetrazolate monohydrate, or barium 2-methyl-5-nitriminotetrazolate dihydrate.¹⁶

Since the copper salts contain chlorine, 7 combusts with a bright blue flame and the water free 8 deflagrates fast (but subsonically) with the formation of a bright blue flame. The ammine complex 9 shows an analogous combustion behaviour to 7. All salts feature no solid residues after their combustion.

The compounds 5–7 were chosen as coloring agents for some pyrotechnic compositions. They offer the possibility of the formation of SrCl, BaCl, and CuCl, respectively – their corresponding light emitting species in the gas phase – without additional chlorine donors. (All other cations used do not need any chlorine for a more intense flame color.) No composition was prepared with 8 and 9, because of their higher sensitivity and the fast deflagration of 8. Furthermore, 9 shows the lowest decomposition temperature. In Table 3 the results of the two best formulations are listed. The performance of each composition has been evaluated with respect to the following categories:

- color emission (subjective impression)
- smoke generation
- morphology and amount of solid residues
- thermal stability
- moisture sensitivity

The US Army red flare composition # 126 A1 (red parachute), 39% Sr(NO₃)₂, 30% Mg, 13% KClO₄, 8% VAAR, was a measure of the red light composition performance. The performance of the compositions for green light were compared to the barium nitrate-based US Army composition # 125 A1 (green parachute): 50% Ba(NO₃)₂, 30% Mg, 15% PVC, 5% VAAR (mass percent). The compositions for blue light were compared with Shimizu's:³¹ 15% Cu, 17% PVC, 68% KClO₄, 5% starch.

The composition 5_1 with the strontium salt 5

Table 3. General summary of the performance of the pyrotechnic composition.

Pyrotechnic composition	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
5_1	+++	++	++	---	-	+++
5_2	+	+	+	---	-	+++
# 126 A1	++	---	++	+++	+++	---
6_1	++	++	++	-	-	-
6_2	+++	+	++	---	-	-
# 125 A1	++	---	++	+++	+++	---
7_1	++	+	+	---	+	++
7_2	+	++	-	-	++	++
Shimizu ³¹	+++	-	++	+++	+++	---

as coloring agent consists of 11% **5**, 44% ADN (ammonium dinitramide), 34% 5-aminotetrazole (**1**) and 11% VAAR. The observed flame color is significantly more intense red compared to that of # 126 A1. Furthermore, the combustion occurs very fast and smokeless. The composition shows high sensitivities towards shock (4.5 J), friction (54 N) and electric discharge (0.75 J). It has a lack in thermal stability ($T_{\text{dec}} = 167\text{ }^{\circ}\text{C}$) and is slightly sensitive towards moisture, but its coloring properties are very good. The mixture **5_2** contains 14% **5**, 68% NH_4NO_3 , 7% Mg and 11% VAAR. The observed flame is intense red, but smaller compared to # 126 A1. The combustion velocity is significantly slower than that of **5_1**. Almost no smoke is produced, but some magnesium sparks could be observed. A very small amount of solid residues was obtained. The decomposition temperature is comparable to **5_1** (165 $^{\circ}\text{C}$), but **5_2** is less sensitive towards shock (6 J), friction (240 N) and electric discharge (1.2 J). Furthermore, it is more stable towards moisture. Figure 6 shows the burn down of all red burning compositions.

The pyrotechnic composition **6_1** containing the barium salt **6** consists of 25% **6**, 45% ADN, 10% **1** and 20% VAAR. It combusts with a very intense green flame (more intense than # 125 A1) and without smoke production. The reaction velocity is comparable to # 125 A1. The sensitivities towards shock (2 J), friction (160 N) and electric discharge (0.65 J) are very high, but similar to **5_1**. Also the decomposition occurs below 180 $^{\circ}\text{C}$ ($T_{\text{dec}} = 175^{\circ}\text{C}$) and the mixture is slightly sensitive towards moisture. Composition **6_2** was made up with 20% **6**, 60% NH_4NO_3 , 4% **1**, 7% magnalium and 9% VAAR. Its flame color is comparably intense to **6_1**, but the burning

**Figure 6.** Burn down of the US Army composition # 126 A1 (top), the compositions **5_1** (middle) and **5_2** (bottom).

velocity is a little slower. As in the case of **5_2** some magnesium sparks and no smoke production could be observed. The combustion occurred completely without solid residues. **6_2** shows the lowest decomposition temperature of 154 °C. It is very sensitive towards shock (4.5 J) and electric discharge (1.0 J), but insensitive towards friction (> 360 N). A comparison of the combustion behavior of the green burning mixtures can be found in Figure 7.

For the preparation of composition **7_1** the copper compound **7** was used (43% **7**, 43% ADN, 4%

starch and 10% VAAR). The observed flame color is comparably intense to that of Shimizu (Figure 8). This is true for the combustion velocity. Smoke could be detected during combustion but less than that of Shimizu and a small amount of solid residues was yielded. The composition **7_1** decomposes at temperatures above 150 °C and is very sensitive towards shock (<1.0 J) and friction (108 N). A marginal sensitivity towards moisture was observed. The pyrotechnic composition **7_2** (24% **7**, 12% ADN, 43% NH₄NO₃, 4% boron and 17% VAAR) shows a less brilliant blue flame color compared to Shimizu's. However, its combustion



Figure 7. Burn down of the US Army composition # 125 A1 (top), the compositions **6_1** (middle) and **6_2** (bottom).



Figure 8. Burn down of Shimizu's composition (top), the compositions **7_1** (middle) and **7_2** (bottom).

occurs smokelessly and with a marginal amount of solid residues. The combustion velocity is slower compared to 7_1. Composition 7_2 offers no sensitivity towards moisture. Its decomposition point is at 159 °C. The sensitivities towards impact and friction were determined to be 2.5 J and 192 N.

Experimental

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^1H and ^{13}C NMR spectra were recorded using a Jeol Eclipse 270, Jeol EX 400 or a Jeol Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards, such as tetramethylsilane (^1H , ^{13}C). To determine the decomposition points of the described compounds a Linseis PT 10 DSC (heating rate β : 5 °C min $^{-1}$) was used. Raman spectra were recorded with a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument, which uses a Nd:YAG laser with a wavelength of 1064 nm. Infrared (IR) spectra were recorded using a Perkin-Elmer One FT-IR instrument with an ATR unit at 25 °C. To measure Elemental Analyses a Netsch STA 429 Simultaneous Thermal Analyzer was employed. The impact sensitivity (E_{dr}) tests were carried out according to STANAG 4489³² modified according to instructions³³ using a BAM (Bundesanstalt für Materialforschung³⁴) drop hammer.³⁵ The friction sensitivity (F_r) tests were carried out according to STANAG 4487³⁶ modified according to instructions³⁷ using the BAM friction tester. The electrostatic sensitivity (E_{el}) tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package”³⁸ For all calorimetric measurements a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb for the combustion of highly energetic materials were used.³⁹

The compounds 1- and 2-(2-hydroxyethyl)-5-aminotetrazole (**2a**, **b**) were prepared according to the literature,^{17,19} as were 1-(2-chloroethyl)-5-aminotetrazole and 1-(2-chloroethyl)-5-nitriminotetrazole.^{19,20}

A solution of 25% vinyl alcohol acetate resin (VAAR) was used as binder (for the pyrotechnic compositions).

Strontium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (5)

A solution of 1.31 g (6.8 mmol) 1-(2-chloroethyl)-5-nitriminotetrazole (**4**) and 0.90 g (3.4 mmol) strontium hydroxide octahydrate in 25 mL H₂O was refluxed for 15 minutes. The solvent was removed under high vacuum to obtain a colorless powder. Recrystallization from H₂O yielded 1.51 g of colorless needles suitable for X-ray determination. Yield: 91%.

Mp 208 °C (dec.). **Raman** (200 mW, 25 °C, cm $^{-1}$): 3016 (6), 2967 (15), 1647 (5), 1542 (3), 1507 (100), 1462 (6), 1438 (6), 1380 (6), 1344 (24), 1291 (7), 1261 (3), 1245 (2), 1205 (3), 1111 (10), 1031 (37), 995 (3), 875 (4), 766 (10), 743 (3), 653 (6), 507 (2), 473 (2), 371 (3), 306 (5), 196 (5). **IR** (Diamond-ATR, cm $^{-1}$): 3501 (w), 3015 (vw), 2966 (vw), 2852 (vw), 2363 (vw), 2340 (vw), 1640 (w), 1508 (m), 1462 (m), 1421 (w), 1380 (s), 1340 (s), 1310 (s), 1257 (m), 1236 (s), 1130 (w), 1109 (m), 1027 (m), 996 (w), 954 (w), 904 (w), 871 (w), 771 (w), 764 (w), 740 (w), 708 (vw), 677 (w), 653 (w). **^1H NMR** (DMSO- d_6): 4.39 (t, 2H, $^3J = 5.9$ Hz, CH₂), 3.98 (t, 2H, $^3J = 5.9$ Hz, CH₂), 3.32 (s, 2H, H₂O). **^{13}C NMR** (DMSO- d_6): 157.7 (CN₄), 47.8 (CH₂), 42.1 (CH₂). **EA** C₆H₁₀Cl₂N₁₂O₅Sr (488.75 g mol $^{-1}$): calc.: C, 14.74; H, 2.06; N, 34.39; found: C, 14.85; H, 2.20; N, 34.62%. $E_{\text{dr}} > 10$ J. $F_r > 360$ N. $E_{\text{el}} > 0.75$ J. $\Delta_c U = -1679$ cal g $^{-1}$.

Barium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (6)

A solution of 1.31 g (6.8 mmol) 1-(2-chloroethyl)-5-nitriminotetrazole (**4**) and 1.07 g (3.4 mmol) barium hydroxide octahydrate in 25 mL H₂O was refluxed for 15 minutes. The solvent was evaporated to obtain a colorless powder. Recrystallization from H₂O–ethanol (1:1) yielded 1.75 g of colorless needles suitable for X-ray diffraction. Yield: 95%.

Mp 207 °C (dec.). **Raman** (200 mW, 25 °C, cm $^{-1}$): 3022 (5), 2974 (12), 1538 (2), 1496 (100), 1460 (4), 1383 (7), 1351 (26), 1315 (6), 1293 (6), 1258 (2), 1199 (1), 1108 (11), 1028 (35), 999 (3), 872 (3), 758 (5), 677 (5), 646 (4). **IR** (Diamond-ATR, cm $^{-1}$): 3607 (w), 3406 (w), 3025 (w), 3002 (vw), 2363 (vw), 2341 (vw), 1783 (vw), 1629 (w), 1496 (m), 1458 (w), 1444 (m), 1429 (m), 1340 (s), 1315 (s), 1258 (m), 1242 (m), 1229 (m),

1136 (w), 1106 (m), 1025 (m), 1000 (w), 961 (vw), 942 (w), 909 (w), 870 (w), 768 (w), 755 (w), 746 (w), 738 (w), 710 (vw), 672 (w), 655 (w), 646 (w). ¹H NMR (DMSO-*d*₆): 4.39 (*t*, 2H, ³*J* = 5.9 Hz, CH₂), 3.98 (*t*, 2H, ³*J* = 5.9 Hz, CH₂), 3.32 (*s*, 2H, H₂O). ¹³C NMR (DMSO-*d*₆): 157.7 (CN₄), 47.8 (NCH₂), 42.1 (CH₂Cl). EA C₆H₁₀Cl₂N₁₂O₅Ba (538.45 g mol⁻¹): calc.: C, 13.38; H, 1.87; N, 31.22; found: C, 13.35; H, 1.85; N, 31.46%. *E*_{dr} > 3.0 J. *F*_r > 144 N. *E*_{el} > 1.0 J. Δ_c*U* = -1512 cal g⁻¹.

***trans*-[Diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato-κ²N⁴,O⁵}copper(II)] dihydrate (7)**

A solution of 2.00 g (10.4 mmol) 1-(2-chloroethyl)-5-nitriminotetrazole (4) in 20 mL H₂O and a solution of 1.21 g (5.2 mmol) copper(II) nitrate pentahydrate in 10 mL H₂O were combined. Deep blue crystals formed after one day of storing at room temperature. Yield: 85%.

Mp 103 °C (loss of H₂O), 242 °C (dec.). **IR** (Diamond-ATR, cm⁻¹): 3649 (w), 3588 (m), 3497 (w), 3168 (s, br), 3031 (s), 2392 (vw), 2286 (vw), 1515 (s), 1463 (s), 1435 (w), 1425 (w), 1383 (s), 1349 (s), 1297 (s), 1268 (s), 1253 (s), 1211 (m), 1138 (w), 1111 (m), 1036 (w), 1010 (w), 959 (w), 904 (w), 872 (w), 810 (w), 772 (w), 764 (w), 740 (m), 684 (w), 662 (w). EA C₆H₁₆Cl₂CuN₁₂O₈ (518.72 g mol⁻¹): calc.: C, 13.89; H, 3.11; N, 32.40; Cl, 13.67; found: C, 13.79; H, 2.90; N, 32.55; Cl, 13.68%. *E*_{dr} > 50 J. *F*_r > 360 N. *E*_{el} > 0.60 J. Δ_c*U* = -1682 cal g⁻¹.

Copper(II) 1-(2-chloroethyl)-5-nitriminotetrazolate (8)

1.00 g (1.9 mmol) *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato-κ²N⁴,O⁵}copper(II)] dihydrate (7) was stored for 48 hours at 110 °C to remove the water of crystallization. 0.84 g of a green powder could be obtained. After recrystallization from half-concentrated HNO₃ bright green crystals suitable for X-ray diffraction could be obtained. Yield: 99%.

Mp 238 °C (dec.). **IR** (Diamond-ATR, cm⁻¹): 3033 (w), 3002 (vw), 2964 (vw), 2360 (w), 2331 (vw), 1739 (w), 1533 (m), 1488 (s), 1452 (m), 1436 (s), 1429 (m), 1388 (w), 1341 (m), 1304 (s), 1235 (s), 1133 (w), 1107 (w), 1047 (vw), 1001 (m), 873 (w), 793 (vw), 775 (vw), 740 (w), 730 (w), 708 (m), 687 (w). EA C₆H₈Cl₂CuN₁₂O₄

(446.66 g mol⁻¹): calc.: C, 16.13; H, 1.81; N, 37.63; found: C, 16.04; H, 1.85; N, 37.60%. *E*_{dr} > 6.0 J. *F*_r > 192 N. *E*_{el} > 0.50 J. Δ_c*U* = -2245 cal g⁻¹.

***trans*-Diammine-bis{1-(2-chloroethyl)-5-nitriminotetrazolato-κ²N⁴,O¹}copper(II) (9)**

At 50 °C 5.0 mL aqueous ammonia solution (25%) were added to a solution of 2.0 g (10.4 mmol) 1-(2-chloroethyl)-5-nitriminotetrazole in 25 mL H₂O. The mixture was combined with a solution of 1.2 g (5.2 mmol) copper(II) nitrate pentahydrate in 10 mL H₂O. The deep blue solution was stored at ambient temperature until deep blue crystals suitable for X-ray diffraction were formed. Yield: 81%.

Mp 205 °C (dec.). **IR** (Diamond-ATR, cm⁻¹): 3332 (w), 3264 (w), 3177 (vw), 1611 (vw), 1512 (m), 1459 (m), 1438 (w), 1396 (s), 1363 (w), 1342 (m), 1301 (w), 1283 (s), 1268 (m), 1234 (s), 1128 (w), 1106 (w), 1026 (w), 991 (vw), 873 (vw), 790 (vw), 766 (vw), 750 (vw), 732 (vw), 708 (w). EA C₆H₁₄Cl₂CuN₁₆O₄ (480.72 g mol⁻¹): calc.: C, 14.99; H, 2.94; N, 40.79; found: C, 15.01; H, 3.13; N, 40.63%. *E*_{dr} = 6.0 J. *F*_r > 360 N. *E*_{el} = 0.50 J. Δ_c*U* = -2495 cal g⁻¹.

Preparation of the pyrotechnic mixtures

For preparation of the pyrotechnic compositions all substances, except the binder, were carefully mixed in a mortar. Then the binder, dissolved in a few millilitres of ethyl acetate, was added. The mixture was formed by hand and dried under high vacuum for several hours. The controlled burn down was filmed with a digital video camera recorder.

Conclusion

In this paper the compounds strontium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (5), barium 1-(2-chloroethyl)-5-nitriminotetrazolate monohydrate (6), *trans*-[diaqua-bis{1-(2-chloroethyl)-5-nitriminotetrazolato-κ²N⁴,O⁵}copper(II)] dihydrate (7), copper(II) 1-(2-chloroethyl)-5-nitriminotetrazolate (8) and *trans*-[diammine-bis{1-(2-chloroethyl)-5-nitriminotetrazolato-κ²N⁴,O¹}copper(II) (9) were presented and extensively characterized using vibrational and multinuclear magnetic resonance spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). Furthermore, their sensitivities

towards shock, friction, and electric discharge and their solubility in H₂O at ambient temperature were determined. The heats of formation were calculated using bomb calorimetric measurements.

The crystal structures of **5**, **6**, **8** and **9** were determined and discussed.

The color performance and combustion properties of all salts **5–9** were analyzed with regard to their usage as potential coloring agents in pyrotechnic compositions.

Furthermore, several pyrotechnic compositions, containing the most promising compounds **5–7**, were prepared and compared to known formulations. They all show promising properties, especially regarding color performance and lower smoke production. The decomposition temperatures and sensitivities towards shock, friction and electric discharge of all prepared pyrotechnic compositions were determined.

Therefore, the prepared salts **5–9** are a step forward in preparing more environmentally benign pyrotechnic compositions without potassium perchlorate.

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 - 28 Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

- 29 E_{dr} : insensitive >40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J;
 F_r : insensitive >360 N, less sensitive = 360 N, sensitive <360 N to > 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N.
 According to the UN Recommendations on the Transport of Dangerous Goods.
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- 33 WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, 2002.
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