Copper in Pyrotechnics

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Abstract: Copper compounds play a key role in the development of "greener" pyrotechnics by substitution of noxious barium compounds from green colored effects. The application of many copper(II) compounds in pyrotechnics is limited because of their noble and often hygroscopic character. We have investigated nitratocuprates(II) as well as basic copper(II) nitrate as potential combined oxidizers and (green) coloring agents. A formulation based on ammonium nitratocuprate(II) nitrate and boron has promising properties for civilian fireworks. Copper-based high-nitrogen compounds show good flame colors as pure compounds. However, the implementation of ready-for-use pyrotechnics from these substances proved to be much more challenging. A promising candidate for civil pyrotechnic applications would be a mixture based on copper(II) nitrate pentahemihydrate and 5-aminotetrazole.

Keywords: cuprates, pyrotechnics, fireworks, green color, pollution

Introduction

Fireworks are no longer the only application of pyrotechnics, since the number of civilian and military applications of pyrotechnics is constantly increasing. Pyrotechnics are used in technological fields such as matches, fire extinguishers, airbags, propellants, all kinds of flares, military countermeasures (acoustic and optical decoy devices), delusion devices and igniters.

In contrast to explosives, pyrotechnics are traditionally mixtures of several compounds. The characteristics of pyrotechnics are consequently dependent on the ingredients and their formulation, which is often determined just by trial and error. Most pyrotechnic reactions are solid-solid state reactions, and the vast number of chemical reactions taking place are not always understood. The basic parts of any pyrotechnic device are the oxidizer and the reductant (fuel). The most common oxidizers are nitrates and perchlorates of alkali and alkaline earth metals. A variety of metals, metalloids or non-metals can be used as a fuel: magnesium, aluminium, magnalium alloy (Mg-Al 50 : 50), titanium, iron, silicon, charcoal, boron, sulfur and many more including

organic compounds and natural products. A binder is usually used to inhibit segregation of the homogeneous, fine-grained mixtures. Coloring agents are used in fireworks and flares.

Colors in pyrotechnics are obtained by the addition of substances with the desired flame color. A vellow flame color is achieved by the addition of sodium compounds, usually cryolite (Na_3AlF_6) or sodium oxalate. The main light-emitting species is atomic sodium. Compounds such as sodium nitrate or sodium chloride are less often used due to their hygroscopic character. In general, compounds used in pyrotechnics should not be hygroscopic nor contain water of crystallization, because water might inhibit the desired reactions or initiate hazardous reactions. Emission of red light is achieved by the addition of strontium nitrate, which simultaneously acts as oxidizer and coloring agent. The same is true for barium nitrate, which is added for green colors. The main emitting species are the monochlorides, SrCl and BaCl, and the monohydroxides, SrOH and BaOH, respectively. Since the above-mentioned chlorides are characterized by a high volatility and satisfactory color emission, such pyrotechnic

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compositions need a chlorine donor: usually perchlorates. PVC powder or other organic or inorganic chlorides. The blue color in pyrotechnics is caused by a copper-chlorine species. There has been a controversy in the literature about the emitting species: Cu₃Cl₃, as suggested in ref. 1 or, more likely, CuCl.² Copper-based coloring agents include metallic copper, copper(1) chloride, basic copper(II) carbonate (azurite and malachite, respectively),copper(II)oxideandcopper(II)sulfide. Basic copper(II) nitrate, Cu₂(OH)₃(NO₃), is known as an additive for gas generating compositions with metal complexes of nitrogen-rich ligands: see the patents in ref. 3-6. However, because of its positive oxygen balance, we investigated its properties as a pyrotechnic oxidizer and colorant. Basic copper(II) nitrate contains both copper and hydroxide which might help form the green lightemitting species CuOH.

Copper compounds sometimes show problematic features that complicate their application in pyrotechnics. In this study, we discuss these features and present an outline of some of the many aspects of copper compounds in pyrotechnics and their role in the recent efforts toward environmentally benign compositions.

Environmental aspects

In several environmental analytical studies as well as medical studies, pyrotechnic applications and fireworks have been identified as potential sources of environmental pollution.⁷ Increasingly rigorous environmental legislation in the industrialized world thus puts pyrotechnicians and the producers of fireworks under pressure to develop alternatives. The environmental legislation may be regarded as exaggerated; however, environmental concerns should be taken seriously and explain recent efforts toward the development of "green" pyrotechnics. Any improvement in this respect will definitely be appreciated by both pyrotechnicians and environmentalists.

The main (potential) pollutants in pyrotechnics are heavy metals (especially barium from green-colored fireworks), perchlorate (which is teratogenic and disturbs the iodine metabolism in the thyroid gland), polychlorinated dibenzo*p*-dioxines (PCDD) and dibenzofurans (PCDF), gaseous pollutants (mainly the oxides of sulfur, nitrogen and carbon; SO_x , NO_x and CO), smoke and particulate matter.⁷

Combustion of organic matter in the presence of chlorine always leads to the formation of traces of toxic and teratogenic PCDD and PCDF. Therefore, pyrotechnics are potential sources of both poisons as well.^{8,9} Interestingly, copper plays a key role in the formation and decomposition of these organohalogen compounds.¹⁰ From this point of view, blue-colored pyrotechnics have been the principal object of investigation in previous environmental studies, since they combine all three factors – organic materials (e.g., the binder), chlorine and copper compounds. In the literature, there is controversy about the significance of pyrotechnics as sources of PCDD/F: Fleischer et al.⁸ conclude that fireworks contribute only marginally to the total output of PCDD/F and can hence be regarded as harmless in this respect (complete absence of the most toxic 2,3,7,8-TCDD), whereas Dyke and Coleman⁹ found a fourfold increase of PCDD/F concentration in ambient air in the course of a night of fireworks and bonfires and believe that fireworks could be a "significant source of dioxins". Fireworks may not contribute to the total PCDD/F output like an industrial waste incinerator; however, the teratogenic character of these substances should be reason enough to not neglect these concerns.

In a study from India, Kulshrestha et al.¹¹ found the barium concentrations in street dust increased by a factor of 1000 immediately after the Diwali festival (the Indian Festival of Lights, which is traditionally accompanied by firecrackers and fireworks), compared to the average value. More than fireworks up in the sky, hand-held flares or indoor fireworks exhibit a severe health-risk for persons standing in the heavy-metal-rich smoke cloud of a green pyrotechnic device. Inhalation of significant amounts of barium aerosols has cardiotoxic and bronchoconstrictor effects.

The development and implementation of bariumfree pyrotechnics is a major challenge for chemists and a field of recent research. Chavez et al.¹² tested green pyrotechnic compositions based on boric acid for application in indoor fireworks. However, they admit that the flame color is of lower quality than in traditional pyrotechnics or barium-containing high-nitrogen compounds. Apart from barium and boric esters, the only elements with a noteworthy green flame color are thallium (one of the most toxic heavy metals) and copper. Of these elements, copper is the least toxic. Occasionally, copper powder or copper compounds like malachite or azurite are added in minor concentrations to greencolored, barium nitrate-based fireworks. Even though many copper compounds are somewhat noxious, their implementation as a substitute for barium compounds can be regarded as an environmental improvement.

Copper-based oxidizers

According to Jennings-White and Kosanke,13 the Cu^{2+} ion is incompatible with magnesium. zinc and aluminium in pyrotechnics, especially in a moist environment. This is the reason why the readily available copper nitrate hydrates $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$ cannot be used in pyrotechnics as oxidizers. Indeed we observed a violent reaction including the emission of brown nitrogen dioxide (NO₂) gas or even selfignition when grinding $Cu(NO_3)_2 + 2.5H_2O$ and magnesium powder in a mortar. The anhydrous covalent copper(II) nitrate, however, is extremely hygroscopic and requires a time consuming synthesis, which makes it unacceptable in pyrotechnics. At the same time, copper(II) compounds do cause problems in pyrotechnics because of their noble character (standard electrode potential for $Cu_{aq}^{2+} + 2e^{-} \rightarrow Cu_s$: $E^0 =$ +0.34 V), e.g. when applied as a coloring agent or as a high-nitrogen fuel copper salt in combination with metal fuels. Thus Cu^{2+} ions act as oxidizers – so why not make use of this trait? The application of water-free, copper(II) oxidizers could be an interesting alternative in the development of green and "green" pyrotechnics.

Tetranitratocuprates(II), $[Cu(NO_3)_4]^{2-}$, have recently been described as suitable pyrotechnic oxidizers.¹⁴ In this patent, the use of cobalt(III)hexaammine nitratocuprate(II), $[Co(NH_3)_6]_2[Cu(NO_3)_4]_3$, as the oxidizer for the inflation of airbags is described. We investigated the applicability of nitratocuprates as both oxidizer and coloring agent for green-colored pyrotechnics.

first fully The structurally characterized nitratocuprate(II) was the nitrosylium compound, NO[Cu(NO₃)₃], previously misinterpreted as the dinitrogen tetraoxide adduct of copper(II) nitrate. Crystal structure analysis confirmed the absence of molecular N₂O₄.^{15,16} In this anion, the Cu²⁺ ions are coordinated by six nitrate ions, where each bridging NO₃⁻ ligand links two copper atoms in an octahedral environment. Later, several tetranitratocuprates were structurally characterized.¹⁷ Some nitratocuprate compounds cocrystallize with one additional metal nitrate moiety, following the general formula $M_3[Cu(NO_3)_4](NO_3)$, where $M = NH_4^+$, K^+ , Rb^+ . The M : Cu ratio is thus 3 : 1.

Experimental

Two nitratocuprates(II) were investigated in the course of this study: the potassium $(K_3[Cu(NO_3)_4](NO_3), KNC)$ and the salt corresponding ammonium salt $((NH_4)_3[Cu(NO_3)_4]$ (NO_3) , ANC). In a previous study, single crystals of both compounds were obtained from the salt melts at elevated temperatures with a large excess of potassium nitrate and ammonium nitrate, respectively.¹⁸ Since this preparation was not practicable for large scale syntheses, we developed an improved synthesis using stoichiometric amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ and the corresponding potassium or ammonium nitrate as solutions in a minimum of concentrated nitric acid (HNO₃, 65%). The excess of nitrate ions inhibits hydrolysis of the $[Cu(NO_3)_4]^{2-}$ complex, following the principle of Le Chatelier. From this solution, water and nitric acid have been evaporated at 110 °C in an oil bath, residual moisture has been removed by heating under high vacuum for 6 hours. A pure product with a yield of 100% was obtained in this simple and straightforward synthesis [see equation (1)].

The resulting product is slightly hygroscopic, but when handled quickly in ambient air, no significant hydrolysis takes place. However, the salts should be stored in air-tight containers and,

$$Cu(NO_3)_2 \cdot 2.5H_2O + 3MNO_3 \xrightarrow{110^{\circ}C/HNO_3} M_3[Cu(NO_3)_4](NO_3) + 2.5H_2O\uparrow$$
(1)
$$M = K^+, NH_4^+$$

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when applied in a pyrotechnic mixture, covered with a non-water-based binder as soon as possible. We mixed pyrotechnic formulations by grinding the constituents in a mortar in the glove box.

Characterization of ANC (as the more promising compound) was performed by single crystal X-ray diffraction via the identification of the crystallographic cell:¹⁸ monoclinic, space group P21/c, a = 8.271(3), b = 14.658(4), c = 12.105(3) Å, $\beta = 90.92(3)^{\circ}$, V = 1467.4(8) Å³); IR (diamond-ATR, cm⁻¹): 3240 (vs), 3071 (sh), 1468 (sh), 1399 (s), 1300 (sh), 1271 (s), 1022 (m), 828 (w), 802 (w), 753 (w); Raman (25 °C, green and blue laser, cm⁻¹, relative intensities given in percent): 1493 (11), 1427 (8), 1337 (5), 1051 (84), 1041 (100), 765 (15), 720 (14), 294 (14), 230 (13); melting point 144 °C (first changes in the crystal morphology), 151–152 °C (true mp). Determination of the melting point was found to be the most practicable way of determining the purity of the water-free product.

Pyrotechnic performance

KNC and ANC were tested in pyrotechnic mixtures with several fuels, additives and vinyl alcohol acetate resin (VAAR) as a binder. The performance was compared to the barium nitrate-based US Army green flare composition # 125A1: 50% BaNO₃, 30% Mg; 15% PVC; 5% VAAR (mass percent). The performance 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
- toxicity of the constituents or reaction products.

Results

The emission of green light is much more intense withANC-based mixtures than withKNC mixtures. The latter obviously lack a sufficient amount of hydrogen to form CuOH, which is the emitting species for the green copper spectrum. ANC mixtures show variable performance, depending on the fuel (see Table 1). Some compositions are very promising for applications in civilian fireworks.

Mixtures of ANC with magnesium and boron powder show the best color performance. Both are even greener than the conventional barium nitrate-based composition (subjective impression when using comparable amounts). Magnesiumfueled compositions ("GST63": 27.3% Mg; 64.5% ANC; 8.2% VAAR), however, offer two major drawbacks – **CAUTION**! – the lack of sufficient thermal stability (self-ignition at 50 °C) and a high moisture sensitivity, which causes selfignition upon storing the pyrotechnic star in moist air or after contact with water. The water-mediated exothermic redox-reaction with magnesium, as described above, is the reason for this undesired

ANC +	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
Mg	+++	+	+			++
Al		+	+	n.d.	n.d.	++
B	+++	+++	+++	-	++	+
Ti		+	+	n.d.	n.d.	++
Si		+++	+++	n.d.	n.d.	++
magnalium	-	+	+	n.d.	n.d.	++
125A1	++			+++	+++	

Table 1. *General summary of ANC-based pyrotechnic compositions, in comparison to the conventional, barium nitrate-based formulation 125A1.*

Key to symbols: +++ outstanding (or large amount of solid residue); ++ good; + fair; - poor; -- bad; --- unacceptable (or very little solid residue); n.d. not determined.



Figure 1. *SEM image of GST90, a boron and ANC-based pyrotechnic formulation.*

self-ignition [equation (2)]. This observation is in good agreement with the warnings of Jennings-White and Kosanke.¹³

$$Mg + Cu^{2+} \xrightarrow{water} \rightarrow Mg^{2+} + Cu + energy \qquad (2)$$

However, compositions based on the use of ANC and boron powder ("GST90": 73.7% ANC; 13.1% boron powder, 325 mesh; 11.3% VAAR; 1% urea; 1% quartz powder), are characterized by a much higher stability. Even in a moist atmosphere, no self-ignition takes place. The quartz powder in the mixture reduces the hygroscopicity of ANC and urea increases the thermal stability to approximately 80 °C. This value may not be enough for military purposes, but is enough for civilian applications, like less toxic indoor fireworks.

This composition burns with a brilliant green flame and generates only very little smoke. The flame color is much more intense compared to the barium-based 125A1 composition. In experiments with flame-color-neutral oxidizers, we observed that the contribution of boron fuel to the green flame color is negligible. Most of the combustion products of GST90 remain as a solid residue in the place of combustion and they keep the shape of the pyrotechnic star before ignition. Water in the composition slightly reduces the combustion velocity. However, the flame color of a star which had been stored in a moist atmosphere for several hours can be described as even more intense than with the very dry product. We believe that the presence of a little water in the mixture facilitates the formation of the emitting species: CuOH. However, the storage of such pyrotechnics in a moist atmosphere should be avoided because of the slightly hygroscopic character of ANC. In the reaction with water, ANC decomposes by the inverse reaction of equation (1), forming copper(II) nitrate pentahemihydrate and ammonium nitrate. Figure 1 shows an SEM image of the composition. One can see that not all grains are covered by the binder, which allows direct contact of some ANC crystallites with the surrounding air. The binder not only suppresses segregation but also, to a certain extent, acts as water sealant of the pyrotechnic. The very dry product is not friction sensitive (>360 N, BAM friction test), but considerably impact sensitive (approximately 2 J, BAM drop hammer).¹⁹ The GST90 composition is less friction sensitive than previously published flash compositions using barium nitrate or potassium perchlorate and metal fuels (60-160 N) and slightly more impact sensitive than those pyrotechnic formulations (5–15 J).²⁰ However, the impact sensitivity of the ANC-boron-based pyrotechnics can be noticeably reduced by a certain amount of moisture in the formulation. So we suggest exposing it to ambient air for approximately 12 hours, before further processing. The dry composition can be ignited by

Table 2. Comparison of the LD_{50} values (oral uptake) of some pyrotechnic ingredients and possible combustion products.

Chemical	LD ₅₀ value/mg kg ⁻¹	Chemical	LD ₅₀ value/mg kg ⁻¹
В	650 (rat)	$Ba(NO_3)_2$	355 (rat)
B_2O_3	3163 (mouse)	$BaCl_2 \cdot 2H_2O$	118 (rat)
B(OH) ₃	2660 (rat)	BaO	50 (mouse)
$Cu(NO_3)_2 \cdot 2.5H_2O$	794 (rat)		
CuO	470 (rat)		

		12	1			
$C_{\rm T}$ (OII) (NO) +	Color	Smokeless	Amount of solid	Thermal	Moisture	Environmental
$Cu_2(OH)_3(NO_3) +$	emission	combustion	residues	stability	stability	compatibility
Mg	+	++	-	++	+++	++
Al			+++	n.d.	n.d.	++
B	-	++	+	n.d.	n.d.	+
Ti		-	++	n.d.	n.d.	++
Si			++	n.d.	n.d.	++
magnalium	-	-	-	n.d.	n.d.	++
S ₈		-	+++	n.d.	n.d.	+

Table 3. General summary of BCN-based pyrotechnic compositions.

electrostatic stimuli only after very intense spark spraying, so this can probably be regarded as a minor threat.

Boron powder is only slightly noxious (hazard symbol Xn – harmful). According to the Material Safety Data Sheet (MSDS), it is an irritant substance and may cause disturbances of the central nervous system. Table 2 summarizes the lethal concentration 50 percent death rate (LD_{50}) for oral uptake of chemicals used in green-colored pyrotechnics and their combustion products.

ANC-boron compositions should not contain chlorine compounds which would cause the emission of blue rather than green light. From environmental point of view, the lack of chlorine offers the advantage that it makes the (potential) formation of toxic polychlorinated organic compounds such as PCDD and PCDF impossible.

Basic copper nitrate $(Cu_2(OH)_3(NO_3), BCN)$ is known as the rare mineral gerhardtite. The natural mineral is orthorhombic, whereas the synthetic compound crystallizes mostly in the monoclinic crystal system.²¹ BCN offers high thermal stability and low hygroscopicity and can be prepared from low cost materials. Furthermore, it is an oxidizer that contains both copper and hydroxide which makes it interesting as a potential coloring agent for pyrotechnic applications for the same reasons mentioned above.

Experimental

 $Cu_2(OH)_3(NO_3)$ was prepared according to literature.²² To a solution of 80 g (1 mol) NH₄NO₃ in 100 mL H₂O, firstly 2.8 g (12 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ in 24.4 mL H2O were added, secondly 12.5 mL of 1.5 M aqueous ammonia solution and lastly 325 mL H2O. The solution was stirred at a temperature of 65 °C for more than 48 hours. During that time it became turbid due to the precipitation of BCN. The light green powder obtained was washed with water and ethanol and dried under high vacuum. Yield: 66%.

IR (diamond-ATR, cm⁻¹): 3540 (s), 3411 (s), 2837 (w), 2739 (w), 2465 (w), 2343 (w), 1762 (w), 1415 (vs), 1349 (s), 1321 (s), 1046 (m), 871 (m), 807 (m), 775 (m), 717 (m), 669 (m); Elemental analysis $Cu_2H_3NO_6$ (240.12 g mol⁻¹): calc.: H, 1.26; N, 5.83; found: H, 1.63; N, 5.88%.

Results

BCN was combined with several fuels and the binder VAAR. The performance was evaluated with respect to the same categories as before (see Table 3).

All compositions with BCN show a poor green flame color. The mixture with magnesium (71.1% BCN; 15.1% Mg; 13.8% VAAR) is comparably the best. Its flame color can be described as pale green. The combustion is almost smokeless and produces only little solid residue. In Differential Scanning Calorimetry (DSC) measurements, the composition starts to decompose at temperatures above 240 °C (heating rate 5 °C min⁻¹). It is also moisture stable.

The flame color achieved in combination with boron powder (53.3% BCN; 26.7% boron powder 325 mesh; 20.0% VAAR) is surprisingly yellow. All other fuels did not yield any flame color. These mixtures were quite hard to ignite and then burned down glowing. Thereby the formation of much smoke and a huge amount of solid residues were observed. For this reason, their stabilities toward temperature and moisture were not determined.

Due to these disappointing results we conclude

that BCN, despite its theoretically good properties, cannot serve as both coloring agent and oxidizer. A mixture of BCN and 5-aminotetrazole fuel verified the applicability of BCN as a gas generant, since we observed no flame but a lot of smoke during its combustion.³

High-nitrogen copper compounds

Nitrogen-rich energetic materials are a rapidly expanding scientific field in the development of new and potentially environmentally benign pyrotechnics.^{7,23} These materials are mostly derivatives of tetrazole and tetrazine. Very often. metal salts and complexes of these substances show a deep flame color of the respective cation (green for Cu^{2+} , in the absence of chlorine) in the flame of a Bunsen burner. However, in many cases, it is difficult to implement these substances pyrotechnic formulations ready-for-use, in because they often drastically forfeit their good coloring performance when pressed into pellets or in combination with a binder or a metal fuel like magnesium. Moreover, they often need an external oxidizer for self-sustaining combustion. It appears that the energetic materials community in many cases ignored these problems related to practical use and settled for the desired flame color of their compounds in the flame of a Bunsen burner. A noteworthy exception is the substantial work of Chavez et al.¹² and Chavez and Hiskey.²⁴ In their investigations, Chavez et al. found that copper(II) compounds in such formulation can exhibit disadvantageous characteristics. A mixture of copper(II) salts in dihydrazino tetrazine (DHT) lacks the long-term stability that is necessary for storage. Furthermore, copper drastically increases the burn rate of DHT and, therefore, should not be used in combination with DHT.



Scheme 1. Structure of the copper(11) $bis(tetrazolyl)amine diammine complex, [Cu(BTA)(NH_3)_2].$

Experimental

We investigated formulations based on the use of copper(II) bis(tetrazolyl)amine diammine ([Cu(BTA)(NH₃)₂], see Scheme 1), a compound that has been developed in our research group.²⁵ The ligand's free acid bis(tetrazoyl)amine hydrate (H₂BTA·H₂O) is synthesized from sodium dicyanamide and sodium azide in diluted hydrochloric acid, ethanol and water.

[Cu(BTA)(NH₃)₂] was prepared according to the literature.²⁵ To a solution of 16.4 g (96 mmol) H₂BTA·H₂O in 500 mL H₂O and 125 mL of concentrated aqueous ammonia solution, 8.2 g (48 mmol) CuCl₂·2H₂O in 50 mL H₂O were added at 70 °C. A blue solid started to precipitate while cooling to 4 °C. The solid was washed several times with ethanol. Yield: 94%.

IR (diamond-ATR, cm⁻¹): 3373 (w), 3321 (s), 3254 (m), 3127 (m), 3053 (m), 2915 (m), 2826 (w), 2656 (vw), 1612 (vs), 1545 (s), 1497 (vs), 1463 (w), 1445 (m), 1327 (w), 1232 (s), 1161 (vw), 1141 (vw), 1123 (w), 1093 (vw), 1017 (vw), 853 (vw), 806 (vw), 746 (m), 723 (m), 675 (w), 620 (vw); Elemental analysis $C_4H_7CuN_{11}$ (248.70 g mol⁻¹):

[Cu(BTA) (NH ₃) ₂] +	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
\dots Mg + MnO ₂	+	+		+++	+++	++
\dots Si + MnO ₂		-	+++	n.d.	n.d.	++
KMnO4		+	+	n.d	n.d.	++
KNO3		+	+	n.d.	n.d.	++
\dots S ₈ + KClO ₃	++		-	+	++	+

Table 4. General summary of $[Cu(BTA)(NH_3)_2]$ -based pyrotechnic compositions.

calc.: C, 9.66; H, 2.84; N, 61.95; found: C, 9.79; H, 3.00; N, 61.40%.

Results

Due to the fact that $[Cu(BTA)(NH_3)_2]$ does not contain any oxygen, the addition of an oxidizer for application in pyrotechnics is essential. Therefore, the performance of potassium permanganate, potassium nitrate and manganese dioxide was investigated. In addition to these mixtures, a composition with potassium chlorate and sulfur was prepared to check the potential of this complex as a blue flame colorant.

Despite the fact that pure $[Cu(BTA)(NH_3)_2]$ powder burns with a beautiful, deep green flame color in the Bunsen burner, the compositions with the potassium salts vielded a bright violet flame color. However, during ignition with a pocket lighter, a green emission could be observed for a short time. The addition of retardant chemicals for lowering the flame temperature, like $KAl(SO_4)_2 \cdot 12H_2O$ or $Cu(SO_4) \cdot 5H_2O$, did not improve the results. Either the same color could be observed as before or the mixture was glowing only. Combinations of $[Cu(BTA)(NH_3)_2]$ with potassium nitrate or permanganate and different fuels like magnesium, silicon and sulfur (all powdered) were disappointing with respect to the emission of green light as well.

Furthermore, [Cu(BTA)(NH₃)₂] was combined with the oxidizer manganese dioxide and the fuels silicon or magnesium powder, respectively. The first mixture burned down by glowing, without any visible flame in any ratio of the constituents. It has long been known that silicon burns with mostly infrared emission only.²⁶ With magnesium fuel and manganese dioxide (24.3% [Cu(BTA) (NH₃)₂]; 66.2% MnO₂; 2.3% Mg; 7.2% VAAR), a spectacular combustion with golden and partly blue sparks could be observed. For this effect, the addition of $[Cu(BTA)(NH_3)_2]$ is essential to obtain a good sparkling result. With an increased amount of magnesium powder, a very bright colorless flame will be obtained. The combustion takes place without generating much smoke; the solid residue is a small amount of brown powder. One major advantage of this pyrotechnic formulation is its stability in a moist environment and at high temperature - it decomposes at temperatures above

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250 °C. Furthermore, it is not impact sensitive (>40 J, BAM drop hammer) nor friction sensitive (>360 N, BAM friction test).

The composition containing $[Cu(BTA)(NH_3)_2]$, sulfur and potassium chlorate produces an intense blue flame. Unfortunately, during the combustion much smoke is produced. Furthermore, it is very sensitive toward impact (<2.5 J, BAM drop hammer) and friction (>80 N, BAM friction test). This fact was expected for a mixture containing sulfur and potassium chlorate. Decomposition occurs at temperatures above 170 °C (DSC, heating rate 5 °C min⁻¹).

For lowering the flame temperature, several mixtures with 5-aminotetrazole fuel were prepared. Copper(II) nitrate pentahemihydrate and bis(2-methyl-5-aminotetrazole)copper(II) nitrate were used as colorant agents and oxidizers and VAAR as a binder. The copper complex diaquabis(1-methyl-5-aminotetrazole)copper(II) nitrate was combined with magnalium alloy and VAAR (for the structures of the tetrazole derivatives, see Scheme 2).

Experimental

The chemicals $Cu(NO_3)_2 \cdot 2.5H_2O$ and 5-aminotetrazole were used as purchased from SigmaAldrich. 1- and 2-methyl-5-aminotetrazole were prepared according to the literature.²⁷

Bis(2-methyl-5-aminotetrazole)copper(II) nitrate $[Cu(2-MeAt)_2(NO_3)_2]_2$ was prepared according



Scheme 2. Structures of 5-aminotetrazole (At), and 1- and 2-methyl-5-aminotetrazole (1-MeAt and 2-MeAt, respectively).

5-Aminotetrazole	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
$ \dots \operatorname{Cu(NO_3)_2} \cdot 2.5 \operatorname{H_2O} + \operatorname{urea} $	+++	+++		+	+	++
$[Cu(2-MeAt)_2(NO_3)_2]_2$	++	++	-	+	++	++
$\frac{[Cu(1-MeAt)_2(H_2O)_2}{(NO_3)_2] + magnalium}$	+	+	++	++	n.d.	++

Table 5. General summary of 5-aminotetrazole-based pyrotechnic compositions.

to Radies.²⁸ A solution of 2.8 g (12 mmol) $Cu(NO_3)_2 \cdot 2.5H_2O$ in 10 mL H₂O was added to a solution of 1.2 g (12 mmol) 2-methyl-5aminotetrazole in 25 mL H₂O at 60 °C. When the dark green solution was allowed to cool down to room temperature, green crystals formed which were washed with ethanol and diethyl ether. After powdering in a crucible, the green powder was dried under high vacuum. Yield: 88.6%.

IR (diamond-ATR, cm⁻¹): 3453 (m), 3352 (s), 3313 (s), 3250 (m), 3173 (m), 2749 (vw), 2357 (vw), 2331 (vw), 1633 (s), 1562 (m), 1536 (m), 1488 (vs), 1458 (s), 1442 (s), 1375 (w), 1295 (s), 1267 (vs), 1198 (w), 1153 (vw), 1124 (vw), 1070 (vw), 1022 (m), 916 (vw), 813 (w), 742 (w), 718 (vw), 647 (w); Elemental analysis $C_4H_{10}CuN_{12}O_6$ (385.79 g mol⁻¹): calc.: C, 12.45; H, 2.61; N, 43.57; found: C, 12.74; H, 2.71; N, 43.12%.

Diaqua-bis(1-methyl-5-aminotetrazole)copper(II) nitrate [Cu(1-MeAt)₂(H₂O)₂(NO₃)₂] was prepared according to Radies.²⁸ A solution of 2.8 g (12 mmol) Cu(NO₃)₂ · 2.5H₂O in 10 mL H₂O was added to a solution of 1.2 g (12 mmol) 1-methyl-5-aminotetrazole in 15 mL H₂O at 60 °C. The dark blue solution was cooled down to ambient temperature. The blue crystals obtained were washed with ethanol and diethyl ether. Yield: 71.3%.

IR (diamond-ATR, cm⁻¹): 3456 (m), 3398 (vs), 3313 (m), 3261 (m), 3203 (m), 3166 (s), 2443 (vw), 1760 (vw), 1647 (m), 1597 (w), 1497 (w), 1420 (m), 1326 (s), 1237 (w), 1139 (vw), 1079 (w), 1050 (w), 984 (vw), 818 (w), 784 (w), 739 (vw), 718 (vw), 689 (w); Elemental analysis $C_4H_{14}CuN_{12}O_8$ (421.78 g mol⁻¹): calc.: C, 11.39; H, 3.35; N, 39.85; found: C, 11.24; H, 3.29; N, 39.25%.

Results

The results of this investigation are listed in Table 5. Only the most promising formulations are listed. The mixture with copper(II) nitrate pentahemihydrate as oxidizer and colorant $(43.7\% \text{ Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}, 43.7\% \text{ At}, 1\%$ urea, 11.6% VAAR) yields the deepest green flame color. It combusts without smoke generation and produces a small amount of solid residues. Urea was added to increase the thermal stability. The mixture decomposes in DSC measurements at temperatures above 130 °C with a heating rate of 5 °C min⁻¹. The stability toward moisture is better than expected. There is no loss in performance after storing it in an open vial for one month.

CAUTION! No magnesium or magnalium alloy should be added to this composition! This causes an explosion even at temperatures as low as 60 °C.

The composition with $[Cu(2-MeAt)_2(NO_3)_2]_2$ as a colorant (45% $[Cu(2-MeAt)_2(NO_3)_2]_2$; 45% 5-aminotetrazole; 10% VAAR) shows a good performance as well. The emitted light is yellowishgreen. Only a small amount of smoke and little solid residue (but more than with the Cu(NO_3)_2 · 2.5H_2O mixture) are formed in the course of combustion. According to DSC measurements (heating rate 5 °C min⁻¹), the mixture decomposes at 148 °C. It is stable toward moisture, but sensitive toward impact (>2.5 J, BAM drop hammer) and friction (>240 N, BAM friction test).

From the observations, we can conclude that 5-aminotetrazole seems to be a good alternative as a fuel if low flame temperature are desirable. This is confirmed by our observations during the investigation of the following pyrotechnics.

A composition containing [Cu(1- $MeAt_2(H_2O_2(NO_3)_2)$] and magnalium alloy (68.4% [Cu(1-MeAt_2(H_2O_2(NO_3)_2], 17.1%)

magnalium, 14.5% VAAR) produces a deep green flame with red spots and no smoke. The red color arises from the formation of CuO in the gas phase which is an indication of a flame temperature too high for the formation of the green light emitter CuOH. One drawback is the afterglow and partial reignition of the solid residue. Surprisingly, $[Cu(1-MeAt)_2(H_2O)_2(NO_3)_2]$, containing water of crystallization, decomposes in combination with magnalium alloy in DSC measurements at temperatures above 152 °C. Sensitivities toward shock, friction and moisture were not determined.

Conclusion

Beyond blue luminescence, copper plays a key role in the development of environmentally benign green-colored pyrotechnics. The noble character and the high hygroscopicity are responsible for the somewhat troublesome features of copper and many copper compounds in pyrotechnics. Until now, copper and copper compounds have been applied almost exclusively as a fuel or as a coloring additive (primarily for blue colors) to a distinct pyrotechnic formulation. To our knowledge, the pyrotechnic composition GST90 presented in this paper (boron + ammonium nitratocuprate(II)) nitrate + binder) is the first including a copperbased combined oxidizer and coloring agent that has been investigated and tested successfully. We could not find a promising composition based on the use of basic copper(II) nitrate to act as both oxidizer and green colorant. High-nitrogen compounds of copper(II), with BTA or derivatives of 5-aminotetrazole as ligands, offer a field for new pyrotechnic investigations. However, it is hard to maintain the good colorant quality of the pure compound in the flame of a Bunsen burner in the course of the production of a material suitable for pyrotechnic applications. Unfortunately, some recent studies on new nitrogen-rich pyrotechnics focused rather on academic problems than on possible applications and problems related to practical use. However, some promising candidates for the application in civilian fireworks (like the mixture of copper(II) nitrate pentahemihydrate and 5-aminotetrazole) have been presented and discussed in this paper.

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