**Blue Emitting Compounds**

**Fine-Tuning: Advances in Chlorine-Free Blue-Light-Generating Pyrotechnics**

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**Abstract:** One of the most challenging tasks in the field of light-producing pyrotechnics is the generation of saturated blue light with high spectral purity. Only copper salts in combination with chlorine seem to be high-performing blue light emitters. However, in modern pyrotechnics the application of chlorine should be avoided. Different strategies are presented to further fine-tune literature-known chlorine-free blue-light-emitting pyrotechnical compositions. The copper iodate as well as the copper bromide systems have been studied by using small amounts of nitrogen-rich compounds like 1,2,4-triazole, 5-amino-1H-tetrazole or 3-nitro-1H-1,2,4-triazole. To overcome sensitivity issues, a two-component epoxy binder system was introduced. The application of both copper(I) iodide and copper(I) bromide in the same pyrotechnical formulation were considered as blue-light-emitting species. Further, a quite new approach by using copper(I) nitrogen-rich coordination compounds was investigated to give a blue flame color. All relevant formulations were characterized with respect to their dominant wavelength and spectral purity as well as impact and friction sensitivity.

**Introduction**

Pyrotechnical disseminated blue light is supposed to be the most challenging color of all.[1] This assumption is not only supported by the limited number of publications, but also by the quite recent steps forward regarding higher spectral purity (SP) and optimized dominant wavelength (DW).[2] Traditionally, a combination of copper salts and chlorine sources were applied to give the desired blue color.[3] Usually, ammonium perchlorate or potassium perchlorate fulfill both the role of an oxidizing agent and as chlorine source.[1,4] In the case of proper flame tuning, the combustion temperature is sufficient to produce the blue light emitter copper(I) chloride. As a result, blue emission in the visible spectrum ranging from 435–480 nm and 428–452 nm with additional peaks between 476–488 nm is observed.[2c] If the temperature exceeds a certain level, the molecular emitter decomposes to give copper(II) oxide and copper(I) hydroxide.[5] CuO can sometimes be spotted as red tip on the top of flame, whereas CuOH emits in the green region and therefore, weakens the overall color quality.[3,6] The formation of the blue light emitter copper(I) chloride is limited by a maximum reaction temperature; for example, Conkling and Shidlovsky supposed 1500 K.[7] Several other temperatures were discussed in the literature, but according to Sturman they should be wrong.[7] Thermodynamic modelling applying the NASA Chemical Equilibria with Applications (NASA-CEA) computer code confirmed Shimizu’s hypothesis that it should be possible to obtain blue compositions of high purity and saturated blue color with copper(I) chloride up to 2500 K.[8] Further increased temperatures should lead to dissociation of copper(I) chloride.

For a long time, it was believed that copper(I) chloride is the only suitable emitter in the blue region. In 2014, Klapötke et al. reported on chlorine-free pyrotechnical mixtures with copper(I) iodide as blue light emitter.[2c] The best working formulation consisted of copper iodate, 5-amino-1H-tetrazole (5-AT), magnesium, copper(I) iodide, and an epoxy binder system (Epon 828/Epikure 3140). To this date, these compositions achieved the highest recorded spectral purity (65 %) and dominant wavelength (473 nm).[2c] In 2015, Juknelevicius et al. outlined another possible blue-light emitter – copper(I) bromide – which was found to achieve SP ≤38 % and DW = 479 nm.[2b] From a toxicity point of view, especially the formulations based on copper(I) iodide are more advantageous, since the postulated formation of highly carcinogenic polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and analogous brominated compounds like polybrominated biphenyls (PBBs) can be avoided.[9] In 2004, the U.S. Department of Health and Human Services summarized earlier publications and indicated that PBBs might accumulate in the environment and were found to cause cancer in selected animal studies.[9c] Potentially formed polyiodinated biphenyls (PIBs) are not believed to be associated with health hazards as they are applied as contrast agents for radiological purposes in medicine, but there are insufficient information given in the literature.[10] Next to halogenated compounds and perchlorates, soluble copper salts tend to show aqueous toxicity and therefore, are considered as part of the problem to create environmentally friendly blue light-generat-
ing pyrotechnical formulations. In 2019, the author’s considered indium as a possible blue light emitter; however, the resulting flame color was dominated by sodium and potassium impurities. Due to the lack of suitable alternatives, the application of copper salts has to be accepted by the military in illumination signals and by the civilian sectors for firework displays or indoor pyrotechnics.

The main task of this presented study was to develop a new pyrotechnic composition that surpasses the performance of known formulations and yields a deep blue color with a DW of 465 ± 20 nm and SP of ≥65%. For this reason, the author’s defined additional requirements for the improvement of newly developed pyrotechnics: The smoke formation should be significantly reduced compared to black powder and only little-produced ash is tolerated. Further, the avoidance of chlorates, perchlorates or other chlorine sources is mandatory. All applied compounds should be commercially feasible, which means sufficient availability to moderate prices. As a consequence, multistep syntheses were not considered for the ongoing investigation. Since all mixtures should be safe in handling, storing and preparing, the sensitivity as well as toxicity should be considered. Regarding the toxicity requirements, compounds with known major toxicity issues were ruled out. Also high amounts of metals and metal salts should be avoided. The safety aspect mainly included the sensitivities towards mechanical stimuli such as impact (IS) and friction (FS). Only formulations which guarantee safe handling are likely to be produced on a larger scale.

Different strategies were applied to achieve the above-mentioned goals, which can be summarized as followed:

- Improvement of the Cu(IO₃)₂ system
- Improvement of the Cu(BrO₃)₂ system
- Copper(I) nitrogen-rich coordination compounds

Results and Discussion

Improvement of the Cu(IO₃)₂ System

The Cu(IO₃)₂ system by Klapötke et al. was chosen as starting point for further investigations. More accurate, the idea was to tune the flame conditions by applying small amounts of nitrogen-rich compounds to increase the spectral purity. The produced nitrogen gas would not only be beneficial to reduced smoke volume, and thus increased spectral purity, but also consumes heat to tailor the flame temperature. This literature-known and proven concept was successfully applied earlier in numerous publications and seemed to be very promising at first.

However, initial experiments applying Cu(IO₃)₂, hexamine, CuBr and nitrogen-rich compounds such as 1,2,4-triazole (Tr), 5-AT, and 3-nitro-1H-1,2,4-triazole (3-NT) only produced brown smoke (see Supporting Information: Table S1, Figure 1). The hint of a small blue flame was only detected at the very beginning of ignition stage and disappeared quickly.

Various other formulations applying guanidine nitrate, copper or urea suffered from stability issues and were not considered for further investigations. As a consequence, the focus shifted to the Cu(BrO₃)₂ system, which was supposed to show bigger potential for improvement regarding the spectral purity and dominant wavelength.

Improvement of the Cu(BrO₃)₂ System

The introduced Cu(BrO₃)₂ system by Juknelevicius et al. achieved lower spectral purities (SP ≤38%) compared to Klapötke’s Cu(IO₃)₂ system as well as the literature-known publication by Shimizu applying undesired potassium perchlorate, copper, poly(vinyl chloride) (PVC) and starch (Table 1).[2c] Shimizu’s formulation shows comparatively high impact sensitivity (8 J), but is less sensitive towards friction.

Table 1. Blue reference formulation S by Shimizu (in wt.-%) and its resulting properties [2b]

| KO₃O₄ | Cu | PVC | Starch | DW /nm | SP /% | IS /J | FS /N |
|-------|----|-----|--------|--------|-------|-------|-------|
| S     | 70 | 10  | 20     | 5      | 475   | 61    | 8     | 324   |

To overcome the disadvantage of low spectral purity, the previously pursued strategy applied for the Cu(IO₃)₂ case was also applied for an analogous Cu(BrO₃)₂ system. In this context, the initial formulations consisted of Cu(BrO₃)₂, hexamine and CuBr only. In the next step, the effect of nitrogen-rich compounds such as Tr, 5-AT and 3-NT was investigated. The amount of introduced nitrogen-rich additive was either 5 wt.-% or 10 wt.-% (Table 2).

All developed formulations showed dominant wavelengths in the desired range of 465 ± 20 nm. The three starting formulations Br₁–Br₃ already exceeded the best formulation by Juknelevicius et al. without incorporating any nitrogen-rich compound.[2b] The addition of Tr, 5-AT and 3-NT further increased the spectral purity up to 50–54 %. Only formulation Br₅ suffered from a reduced spectral purity compared to the formulations Br₁–Br₃. It is noteworthy that, upon burning of formulation Br₉, no residue was left at all (Figure 2).

Unfortunately, the sensitivities towards mechanical stimuli increased to a non-tolerable level (Table 2). According to the Bundesanstalt für Materialforschung (BAM), the friction sensitivity of formulations Br₁–Br₃ was characterized as very sensitive and changed for the worse with addition of nitrogen-rich additives.[15] It was discovered that a higher amount of additive resulted in higher sensitivity and safety risk. Whereas formula-
Table 2. Cu(BrO$_3$)$_2$-based formulations Br1−Br9 (in wt.-%) and their resulting properties.

| No. | Cu(BrO$_3$)$_2$ | Hexamine | CuBr | Tr | 5-AT | 3-NT | DW /nm | SP /% | IS /J | FS /N |
|-----|----------------|----------|------|----|------|------|--------|-------|------|-------|
| Br1 | 70             | 10       | 20   | –  | –    | –    | 465    | 44    | 2    | 30    |
| Br2 | 70             | 15       | 15   | –  | –    | –    | 468    | 40    | 7    | 36    |
| Br3 | 65             | 15       | 20   | –  | –    | –    | 466    | 46    | 8    | 40    |
| Br4 | 65             | 10       | 20   | 5  | –    | –    | 468    | 52    | 10   | 20    |
| Br5 | 65             | 10       | 20   | –  | 5    | –    | 464    | 39    | 8    | 20    |
| Br6 | 65             | 10       | 20   | –  | –    | 5    | 467    | 54    | 3    | 16    |
| Br7 | 60             | 10       | 20   | 10 | –    | –    | 468    | 50    | 1    | 16    |
| Br8 | 60             | 10       | 20   | –  | 10   | –    | 468    | 50    | 1    | 16    |
| Br9 | 60             | 10       | 20   | –  | –    | 10   | 470    | 53    | 1    | 18    |

Table 3. Selected Cu(BrO$_3$)$_2$ based formulations (in wt.-%) and their resulting properties.[a]

| No. | Cu(BrO$_3$)$_2$ | Hexamine | CuBr | Tr | 5-AT | 3-NT | Binder | DW /nm | SP /% | IS /J | FS /N |
|-----|----------------|----------|------|----|------|------|--------|--------|-------|------|-------|
| Br12| 60             | 15       | 20   | –  | –    | –    | 463    | 50    | 3    | 24    |
| Br15| 55             | 15       | 20   | –  | –    | –    | 467    | 50    | 2    | 32    |
| Br18| 60             | 20       | 15   | –  | –    | 5    | 464    | 48    | 2    | 18    |
| Br21| 60             | 10       | 20   | –  | –    | 10   | 468    | 54    | 3    | 42    |
| Br33| 65             | 10       | 20   | –  | 5    | –    | 469    | 50    | 4    | 14    |
| Br34| 65             | 10       | 20   | –  | 5    | 8    | 470    | 49    | 5    | 18    |
| Br37| 60             | 10       | 20   | 10  | –    | 5    | 468    | 53    | 2    | 48    |
| Br38| 60             | 10       | 20   | 10  | –    | 8    | 469    | 47    | 1    | 36    |
| Br41| 60             | 10       | 20   | –  | 10   | 5    | 470    | 48    | 2    | 36    |
| Br42| 60             | 10       | 20   | –  | –    | 10   | 465    | 44    | 3    | 30    |

(a) Binder = Epon 813/Versamid 140 (4:1); weight percentage in total = 100 wt.-% + 5–8 wt.-% binder = 105–108 wt.-% per formulation.

Formulations Br19–Br30 were prepared to investigate the effect of slightly increased amounts of CuBr (max. 25 wt.-%), while keeping the oxidizer level constant (see Supporting Information: Table S4). Br19, Br20, Br22–Br25, and Br30 also showed a red tip and therefore, were excluded from further investigations. Only Br21 was further characterized and classified as sensitive towards impact and friction (Table 3). During the grinding step, formulations Br26 to Br29 accidently decomposed with a big flame and crackling sound. It was assumed that these formulations were even more sensitive than previous compositions.

Even though the spectral purities of these formulations increased up to 54 % and also fulfilled the requirement for dominant wavelength, the resulting sensitivities were considered as a serious problem. One literature-known strategy to reduce the sensitivity of pyrotechnical formulations is the addition of non-energetic binder materials such as carbohydrates, oils or epoxy resins.[16] These binder materials usually do not only increase the mechanical stability of the pressed pellet, but also coat the particles, which further should reduce the sensitivity by minimizing the emerging shearing forces.[16b] However, the burning behavior as well as optical properties can also be influenced by binder systems. The binder itself can act as fuel providing more heat to the combustion process and thus, alter the resulting combustion temperature. Br31–Br42 were prepared to study the effect of an epoxy binder system (Epon 813/Versamid 140, 4:1) on the occurring properties (see Supporting Information: Table S5).

The spectral purity of Br31, Br32, Br35, Br36 and Br40 dropped to 39–43 % and therefore, these formulations were excluded from further investigations. The same compositions with additional 5–8 wt.-% binder did not reveal the intended effect of reduced sensitivity (Table 3). Quite contrary to the expecta-
tions, the sensitivities of formulations Br37 and Br38 surprisingly increased with higher binder content. This phenomenon might be explained by the altered stoichiometry resulting in higher reactivity. A comparison of the pair Br33 and Br34 indicated only a slight loss in sensitivity, which might be negligible due to measurement errors. For Br41 and Br42, an increase of friction sensitivity was accompanied by a small decrease in the sensitivity towards impact. It is obvious that in this case there is no connection between the binder content and the formulation's resulting sensitivity performance.

It has to be stated that especially the grinding process of all solid materials turned out to provide the highest risk for accidental decomposition. Other methods for safe sample preparation have to be considered in the future. Grinding and coating every single component separately before wet-mixing the ingredients might be an option for further investigations. However, the sensitivities in a dry state of these so-prepared formulations are questionable.

Finally, compositions applying a minimum content of metal or metals salts were developed to meet the above-introduced requirements for modern pyrotechnics. Br11 provides a blue formulation applying minimum amounts of copper or copper salts by using potassium bromate (KBrO3) as an oxidizing agent (Table 4).

The halogen source of choice was ammonium bromide NH4Br as well as Cul. In combination with elemental copper, the blue light was generated by a mixture of two emitters – copper(I) bromide and copper(I) iodide. Unfortunately, the impact sensitivity was found to be one of the most hazardous ones; therefore, a spontaneous decomposition during the manufacturing process is very likely. As a result, these kinds of pyrotechnical mixtures were excluded from further investigations. How
erever, the sensitivities in a dry state of these so-prepared formulations are questionable.

Copper(I) Nitrogen-Rich Coordination Compounds

The performance of pyrotechnical formulations is influenced by a lot of factors, e.g. environmental factors, sample preparation or material shape.[8,9b] Small deviations in the production step, chemicals from another supplier or even different batches of the same supplier can cause big effects on the resulting performance and require a batch-to-batch reformulation.

To overcome the inconsistencies arising from mixing of several powders, the idea was to reduce the number of ingredients by combining the colorant, oxidizer and fuel in just one molecule.[17] Analogue to the tetrakis(acetonitrile) copper(I) perchlorate complex published by Csöregh et al. in 1974, the first step was to synthesize the tetrakis(acetonitrile) copper(I) periodate complex (Scheme 1). In a second step, the corresponding tetrakis(acetonitrile) copper(I) periodate complex with various nitrogen-rich compounds as stabilizing ligands should be obtained via metathesis reaction.[18]

$$\text{Cu}_2\text{O} + 2\text{H}_2\text{O}_6 + \text{MeCN} \rightarrow 2\text{[Cu(MeCN)]IO}_4 + 5\text{H}_2\text{O}$$

Scheme 1. Planned synthetic route to [Cu(MeCN)]IO4 with N-rich ligand = 5-amino-1-methyl-1H-tetrazole (1-MAT); 5-amino-2-methyl-2H-tetrazole (2-MAT); 1,5-diaminotetrazol (1,5-DAT).

A mixture of periodic acid and acetonitrile was provided. Subsequently, Cu2O was added and heated until a clear solution was observed. This so-prepared solution was allowed to stand in air for crystallization. Unfortunately, all solutions turned blue and the intended complex could not be observed in the elemental analysis.

The blue color already indicated the formation of copper(II) salts. In an attempt to overcome the occurring oxidation process, the nitrogen-rich ligands were first dissolved in periodic acid resulting in the same color shift (Scheme 2).

Scheme 2. Attempts at preparing copper(II) complexes.

The tetrakis(acetonitrile) copper(I) periodate could not be isolated. Furthermore, 1,5-DAT instantly decomposed upon addition to the periodic acid solution, which was indicated by an instant gas formation. For the ligands 1-MAT and 2-MAT, a mixture of green and blue solid material was obtained after crystallization. The solution applying 1-MAT showed small colorless crystals in the glass vessel. X-ray analysis proved the formation of the corresponding 1-MAT periodate salt instead of the intended product. It was concluded that the formation of [Cu(N-rich ligands)]IO4 complexes is not possible by applying the literature-stated procedure for analogous perchlorate complexes. Due to the blue colored solution, the copper(I) ions were oxidized to copper(II) during the reaction. The oxidizing properties of periodic acid already decomposed one N-rich ligand.
upon addition, which further reduces the number of possible compounds for future investigations.

Domyati et al. reported on copper(I) complexes with pincer N-heterocyclic carbene (NHC) ligands starting from the reaction of \([\text{Cu(MeCN)}_4]PF_6\) or \([\text{Cu(MeCN)}_4]SbF_6\) and an in situ generated NHC at room temperature in the absence of air and moisture.\(^{[19]}\) Consequently, other tetrakis(acetonitrile) copper(I) complexes with varying anions are known, which might serve as starting materials for simple metathesis reaction to obtain \([\text{Cu(MeCN)}_4]IO_4\).

Some of them are already commercially available, e.g., \([\text{Cu(MeCN)}_4]^+ Y\) with \(Y = \text{SbF}_6^–, \text{BF}_4^–, \text{ClO}_4^–, \text{PF}_6^–\). Acetonitrile (MeCN) is a weakly coordinated ligand, which can be substituted by stronger coordinating ligands such as triphenylphosphine (PPh₃) as well as bidentate ligands like diphenylphosphinomethane (dppm) or 1,10-phenanthroline (phen).\(^{[20]}\) Most of the reported copper(I) complexes are also moisture- or air-sensitive; therefore, they cannot be considered in any pyrotechnical formulation.\(^{[21]}\)

Further attempts to synthesize the \([\text{Cu(MeCN)}_4]IO_4\) complexes starting from the commercially available compound \([\text{Cu(MeCN)}_4]BF_4\) via metathesis reactions failed (Scheme 3). In this study, it was not possible to successfully introduce copper(I) complexes in blue-light-emitting pyrotechnical formulations. Finally, it was concluded that copper(I) complexes need further research as well as improvement to meet the stability and sensitivity requirements for the application in modern pyrotechnical systems.

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\begin{align*}
V. & \quad [\text{Cu(MeCN)}_4]BF_4 + \text{H}_3\text{IO}_6 (aq.) \xrightarrow{\text{MeCN} \quad 90 ^\circ \text{C} \quad 2 \text{H}_2\text{O}} 2[\text{Cu(MeCN)}_4]IO_4 + \text{H}^+ + \text{BF}_4^- \\
VI. & \quad [\text{Cu(MeCN)}_4]BF_4 + \text{NaIO}_4 \xrightarrow{\text{MeCN} \quad 90 ^\circ \text{C} \quad 2 \text{H}_2\text{O}} 2[\text{Cu(MeCN)}_4]IO_4 + \text{NaBF}_4
\end{align*}
\]

Scheme 3. Failed metathesis reactions applying \([\text{Cu(MeCN)}_4]BF_4\).

Conclusions

In the presented work, three different strategies are discussed to further fine-tune the performance of literature-known blue-light-emitting pyrotechnical compositions. The author’s defined several requirements for these modern mixtures. The most important one is that the formulation should provide a deep blue color with a dominant wavelength of 465 ± 20 nm and spectral purity of ≥65 %.

The first approach was the improvement of the most-promising \([\text{Cu(O}_3\text{I)}_2]_2\) system, however, it was not possible to generate a blue flame and most of the mixtures suffer from stability issues. As a result, the focus shifted to the fine-tuning of the \([\text{Cu(O}_3\text{I)}_2]_2\) system. The author’s summarized the optical performance and the corresponding impact and friction sensitivity of discussed formulations together with Shimizu’s blue reference and Juknelevicis’ \(\text{KBrO}_3\) system in an overview (Figure 3).\(^{[2b,3]}\)

The literature-known \(\text{KBrO}_3\)-based formulation reached only a spectral purity of ≤38 %. The flame conditions were tailored with nitrogen-rich compounds – 1,2,4-triazole, 5-amino-1\(H\)-tetrazole and 3-nitro-1\(H\)-1,2,4-triazole – to reduce smoke generation, increase spectral purity and control temperature. With this strategy spectral purities up to 54 % could be observed. Unfortunately, these mixtures suffer from impact and friction sensitivity (IS: 1–5 J, FS: 14–48 N), whereby a safe manufacturing process cannot be guaranteed. Also the addition of a two-component binder system was not able to reduce the sensitivity against mechanical manipulation. However, the authors proved that it is possible to reach the optical performance of Shimizu’s perchlorate-based blue reference formulation (SP: 61 %, DW: 475 nm, IS: 8 J, FS: 324 N) with the fine-tuning of bromate-based mixtures. The application of both blue-light-emitters copper(I) bromide and copper(I) iodide was excluded from further investigation, because of sensitivity issues.

The last concept to improve the performance of blue-light-emitting pyrotechnics was the addition of copper(I) nitrogen-
rich coordination compounds served as colorant, fuel and gas generator in one molecule. Due to stability and sensitivity issues, it was not possible to introduce copper(I) complexes to pyrotechnical mixtures.

Experimental Section

CAUTION! The described pyrotechnical mixtures might explode during preparing, handling or manipulating! They are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. Please handle these materials with care! Precautionary measures are mandatory and protective equipment like safety glasses, face shields, leather coats, Kevlar® gloves, and ear protectors is highly recommended.

Chemicals. The following materials were used as provided without further purification: 5-amino-1H-tetrazole (98 %), abcr Chemicals; 1,2,3-triazole (99.5 %), Acros Organics; 3-nitro-1H-1,2,4-triazole (97 %), Sigma-Aldrich; Hexamethylenetetramine (99.5 %), abcr Chemicals; copper (–40+100 mesh, 99.5 %), Alfa Aesar; ammonium (97 %), Sigma-Aldrich; Kevlar® gloves, and ear protectors is highly recommended.

Sample Preparation. All pyrotechnic samples were prepared in 1.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to literature procedures or provided at the laboratory stock.

Optical Measurements. Optical emissive properties were characterized using both an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm) and an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm). The optical characteristics were measured using both an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm) and a detector-sample distance of 1.0 m and an acquisition time of 5 °C min–1.

Synthesis of copper(I) complexes

Route (I): Synthesis of copper(I) complexes for each formulation and all given values are averaged based on nant C as the white reference point. Five samples were measured.

Sample Preparation. All pyrotechnic samples were prepared in 1.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to literature procedures or provided at the laboratory stock.

Optical Measurements. Optical emissive properties were characterized using both an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm) and an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm). The optical characteristics were measured using both an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm) and a detector-sample distance of 1.0 m and an acquisition time of 5 °C min–1.

Synthesis of copper(I) complexes

Route (I): A mixture of periodic acid (2 m, 5 mL) and acetonicitrile (15 mL) was prepared. Subsequently, Cu2O (71.6 mg, 0.05 mmol) was added and heated (50 °C) until a clear solution was observed. After crystallization on air, the solution turned blue. A blue-greenish precipitate was obtained after removal of the solvent. EA (C8H12N4O4CuI, 418.66 g mol–1) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.00, N 0.00 %.

Route (II)–(IV): The nitrogen-rich ligands (200 mg, 4 equiv.) were dissolved in a mixture of periodic acid (2 m, 5 mL) and acetonicitrile (15 mL). After addition of Cu2O (1 equiv.), the solution was heated (50 °C) until all solid material was dissolved. The solution was allowed to stand on air for crystallization. A blue-greenish precipitate was obtained after removal of the solvent. EA (C8H12N4CuI, 418.66 g mol–1) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.00, N 0.00 %.

Route (V)–(VI): [Cu(MeCN)4]BF4 (200 mg, 0.62 mmol) was dissolved in an excess of acetonicitrile (15 mL) and heated (50 °C) until a clear solution was observed. Upon addition of one droplet of H3IO2 (2 mL), a green precipitate occurred immediately. EA (C8H12N4O4CuI, 418.66 g mol–1) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.00, N 0.00 %.

Sensitivity Data. The impact and friction sensitivities were determined using a BAM DropHammer and a BAM Friction Tester. The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+), Impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J. The thermal stability was carried out using an OZM Research DTA 552 Ex Differential Thermal Analyzer with a heating rate of 5 °C min–1.

Acknowledgments

For financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR.N00014-16-1–2062 and the Strategic Environmental Research and Development Program (SERDP) under contract no. WP19–1287 are gratefully acknowledged. The author’s thank Mr. Marcel Holler for taking photos. We are also grateful to Mr. Stefan Huber for sensitivity measurements.

Keywords: Blue emission, Copper, Photophysics, Pyrotechnics

[1] R. Lancaster, Fireworks, Principles and Practice, Chemical Publishing Company, New York City, NY, USA, 1998.
[2] a) D. Juknelevicius, A. Duffer, M. Rusan, T. M. Klapotke, A. Ramanavicius, Eur. J. Inorg. Chem. 2017, 1113–1119; b) D. Juknelevicius, E. Karvinen, T. M. Klapotke, R. Kubilius, A. Ramanavicius, M. Rusan, Chem. Eur. J. 2015, 21, 15354–15359; c) T. M. Klapotke, M. Rusan, J. J. Sabatini, Angew. Chem. Int. Ed. 2014, 53, 9665–9668; Angew. Chem. 2014, 126, 9820.
[3] T. Shimizu, Fireworks: The Art, Science, and Technique, Pyrotechnica Publications, Austin, Texas, USA, 1996.
[4] a) A. Hardt, B. L. Bush, T. Shimizu, B. T. Neyer, Pyrotechnics Pubns, Corozal, PR, USA, 2001; b) R. Webb, A. von Oertzen, S. Myatt, D. Chapman, M. P. van Rooijen, W. Colpa, E. G. de Jong, C. de Ruiter, Chapman, M. P. van Rooijen, W. Colpa, E. G. de Jong, C. de Ruiter, Literature review of fireworks compositions, propagation mechanisms, storage legislation and environmental effects, Bundesanstalt für Materialforschung und -prüfung, EVG1-CT-2002-00074 ChAF, Berlin, Germany, 2003.
[5] B. E. Dowda, Theory of Colored Flame Production, Naval Sea Systems Command Crane, ADA951815, Crane, IN, USA, 1964.
[6] M. Russell, The Chemistry of Fireworks, The Royal Society of Chemistry, Cambridge, UK, 2009.
[7] B. T. Sturman, Propellants Explos. Pyrotech. 2006, 31, 70–74.
[8] a) NASA Glenn Research Center, NASA Computer program CEA (Chemical Equilibrium with Applications) Code, https://www.grc.nasa.gov/www/CEA-Web/, Cleveland, OH, USA, 2017; b) T. Shimizu, Fireworks from a physical standpoint, Pyrotechnica Publications, Austin, TX, USA, 1981.
[9] a) W. Christmann, D. Kasiske, K. D. Klöppel, H. Partscht, W. Rotard, Chemosphere 1989, 19, 387–392; b) O. Fleischer, H. Wichmann, W. Lorenz, Chemosphere 1999, 39, 925–932; c) Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers, Department of Health and Human Services, Public Health Service, Atlanta, GA, USA, 2004.

[10] K. Thomson, D. K. Varma, Aust. Prescr. 2010, 33, 3537.

[11] G. Weingart, Pyrotechnics, Bloomfield Books, Portland, ME, USA, 1998.

[12] J. Glück, T. M. Klapötke and T. Küblböck, The Flame Emission of Indium from a Pyrotechnical View, Z. Anorg. Allg. Chem. 2019, (accepted: DOI: https://doi.org/10.1002/zaac.201900185).

[13] a) J. A. Conkling, C. Mocella, Chemistry of Pyrotechnics: Basic Principles and Theory, CRC Press, Boca Raton, FL, USA, 2010; b) T. M. Klapötke, Chemistry of High-Energy Materials, Boston: De Gruyter, Berlin, Germany, 2017.

[14] a) D. E. Chavez, M. A. Hiskey, J. Pyrotech. 1998, 11–14; b) D. E. Chavez, M. A. Hiskey, D. L. Naud, J. Pyrotech. 1999, 17–36; c) I. E. Drukenmüller, T. M. Klapötke, Y. Morgenstern, M. Rusan, J. Stierstorfer, Z. Anorg. Allg. Chem. 2014, 640, 2139–2148; d) J. Glück, T. M. Klapötke, M. Rusan, J. Stierstorfer, Chem. Eur. J. 2014, 20, 15947–15960; e) T. M. Klapötke, T. G. Müller, M. Rusan, J. Stierstorfer, Z. Anorg. Allg. Chem. 2014, 640, 1347–1354.

[15] a) BAM Bundesanstalt für Materialforschung und -prüfung, Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien, Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany, 2015; b) Committee of Experts on the Transport of Dangerous Goods, UN Recommendations on the Transport of Dangerous Goods, United Nations Economic and Social Council, New York City, NY, USA, 2019.

[16] a) F. M. Betzler, V. A. Hartdegen, T. M. Klapötke, S. M. Sroll, Cent. Eur. J. Energ. Mater. 2016, 13, 289–300; b) J. J. Sabatini, C. T. Freeman, J. C. Poret, A. V. Nagori, G. Chen, Propellants Explos. Pyrotech. 2011, 36, 145–150.

[17] L. H. Blair, A. Colakel, R. M. Vrcelj, I. Sinclair, S. J. Coles, Chem. Commun. 2015, 51, 12185–12188.

[18] I. Csöregh, P. Kierkegaard, R. Norrestam, Acta Crystallogr., Sect. A 1975, 31, 314–317.

[19] D. Domyati, S. L. Hope, R. Latifi, M. D. Hearns, L. Tahsini, Inorg. Chem. 2016, 55, 11685–11693.

[20] T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, Chem. Commun. 2000, 1689–1690.

[21] a) V. A. de Lucca Neto, A. E. Mauro, V. Sargentelli, M. Ionashiro, Thermochem. Acta 1995, 260, 235–241; b) H.-C. Liang, K. D. Karlin, R. Dyson, S. Kaderli, B. Jung, A. D. Zuberbühler, Inorg. Chem. 2000, 39, 5884–5894; c) H.-C. Liang, E. Kim, C. D. Incarvito, A. L. Rheingold, K. D. Karlin, Inorg. Chem. 2002, 41, 2209–2212; d) T. N. Sorrell, D. L. Jameson, J. Am. Chem. Soc. 1982, 104, 2053–2054.

Received: October 14, 2019