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Copper(II) Chlorate Complexes – the Renaissance of a Forgotten and Misjudged Energetic Anion

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ABSTRACT: A convenient synthetic route toward new copper(II) chlorate complexes with potential use in modern advanced ignition or initiation systems is described. Obtained compounds were not only accurately characterized (XRD, IR, UV/Vis EA and DTA) but also investigated for their energetic character (sensitivities, initiation capability and laser ignition). The copper 4-aminotriazolyl chlorate complex showed excellent initiation of PETN, while also being thermally stable and safe to handle. Solid-state UV-Vis measurements were performed to get a possible insight toward the laser initiation mechanism. In contrast to expectations, the presented copper(II) chlorate energetic coordination compounds show manageable sensitivities that can be tamed or boosted by the appropriate choice of nitrogen-rich ligands.

The use of chlorates is still ever-present in everyday life with applications in bleach (both NaClO_3 and KClO_3 are responsible for the production of ClO_2 in elemental chlorine-free bleaching processes), oxygen candles (for aircrafts or submarines), herbicides and even medicine (e.g. $\text{Al}(\text{ClO}_3)_3$ in mouth washes against mild inflammation in the pharynx due to its astringent effect).¹ The mixture of approx. 65–80 w% potassium chlorate together with 20–35 w% red phosphorus in one of the most spectacular and sensitive formulations, called the *Armstrong's mixture* (Figure 1A), can cause disastrous accidents. The composition tends to spontaneously ignite when mixed or grinded. It is used in matches, fireworks, toy cap guns and earlier in primers and guns. It has nearly been completely replaced due to corrosion issues. Also, the risk of misuse is high and may lead to accidents through incorrect handling.² Mixtures containing chlorates with different reducing agents such as sugar, metal powders, saw dust, carbon black or graphite are extremely dangerous.³ Chlorates possess a high oxidation potential (performance), are thermally stable ($T_{\text{dec.}}$ NaClO_3 : 255 °C, KClO_3 : 368 °C) and show low toxicities (LD_{50} (NaClO_3) 1200 mg kg^{-1}).⁴ Investigations by the European Food Safety Authority showed that the potency of chlorate to the human body is 10 times lower compared with perchlorate and only chronic exposure over a long time period could cause inhibition of the thyroid iodine uptake.⁵ The ongoing use of lead containing priming mixtures and the accompanied environmental accumulation holds a high ecological risk. Finally, lead styphnate and lead azide, the most commonly used substances in primer mixtures, were put on the candidate list of authorization (substances of very high concern, Annex XIV) during the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals)⁶ regulations in 2011 due to their

high toxicity. This could lead to prohibition or restriction of the compounds, which makes research into possible alternatives very important.⁷

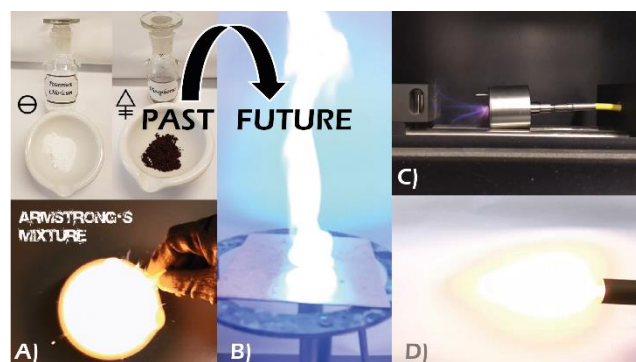
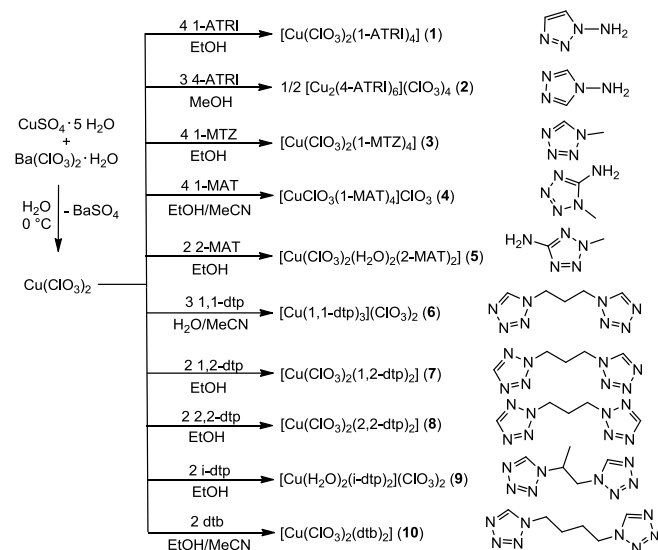


Figure 1. Old versus new: A) Armstrong's mixture containing potassium chlorate and red phosphorus; B) hot plate test showing blue light emission during the decomposition from copper(II) chlorates; C) laser ignition of a copper(II) chlorate complex 8; D) smokeless muzzle flash of a new ignition mixture.

The described approach herein for the replacement of lead containing primary explosives is the use of energetic copper(II) chlorate complexes, which were stabilized and tuned with different endothermic nitrogen-rich ligands. Interestingly, very few copper(II) complexes using chlorate as the counter-anion or ligand have been described in literature. These include ammonia, a few primary amines, ethylenediamine and 4-amino-1,2,4-triazole (4-ATRI).⁸ However, crystal structures and sensitivities have not been reported and energetic investigations are limited to their decomposition temperatures. This may be a consequence

of the poor accessibility toward copper(II) chlorate, which is not commercially available, exists with variable water contents (4–6 H₂O) and is highly hygroscopic.⁹ Although perchlorates are stronger oxidizers, the reduction of chlorates is favored, leading to an easier initiation.¹⁰ The higher reactivity can also be explained by the missing shielding of the chlorine(+V) atom. The difficult but main goal in the synthesis of metal chlorate complexes is the stabilization of the desired products. For that reason, neutral tri- and tetrazole derivatives were utilized, which are either commercially available or easy to synthesize.¹¹ The next challenge we faced was the difficult access to copper(II) chlorate, which was solved by a simple metathesis reaction and exploiting the precipitation of barium sulfate as the driving force (Scheme 1). Due to the high hygroscopicity of copper(II) chlorate, freshly prepared alcoholic solutions (except **6**) of copper(II) chlorate were combined with respective stoichiometric amounts of the ligands dissolved in organic solvents (MeOH, EtOH, MeCN).

Scheme 1. Synthesis of the complexes 1–10 starting from copper(II) sulfate and barium chlorate



Overview of used nitrogen-rich ligands: 1-ATRI: 1-amino-1,2,3-triazole; 4-ATRI: 4-amino-1,2,4-triazole; 1-MTZ: 1-methyltetrazole; 1-MAT: 1-methyl-5-aminotetrazole; 2-MAT: 2-methyl-5-aminotetrazole; 1,1-dtp: 1,3-di(tetrazol-1-yl)propane; 1,2-dtp: 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane; 2,2-dtp: 1,3-di(tetrazol-2-yl)propane; i-dtp: 1,1'-(propane-1,2-diyl)bis(tetrazole); dtb: 1,4-di(tetrazol-1-yl)butane.

All compounds were analyzed by low temperature single crystal X-ray diffraction. Figure 2 shows six different coordination modes in the complexes with no (**2**, **6** and **9**), one (**4**) and two (**5** and **8**) coordinating chlorato ions. The most favored mode in this study is the octahedral coordination sphere with two coordinating chlorato ligands surrounding the copper(II) metal center. Also, an extraordinary square pyramidal coordination in compound **4** with both a coordinating chlorato ligand and a non-binding chlorate counter-anion was observed. Monodentate ligands such as 1-ATRI, 1-MTZ, 1-MAT and 2-MAT lead to the formation of closed octahedral coordination spheres in the complexes **1** and **3–5**. Whereas 4-ATRI and the propyl-linked ditetrazole

isomers are bidentate and form 1D polymeric chains by coordinating between the same copper(II) cation in compounds **2** and **6–9**. A different situation can be found in complex **10**, where each butyl ligand bridges two different center metals forming 2D polymeric networks. While complexes **2** and **6** are the only presented compounds with copper(II) ions exclusively coordinated by six nitrogen donors, the coordination sphere of **5** shows the greatest variety with two aqua, chlorato and tetrazole ligands each. The molecular unit of **2** consists of two different crystallographic center atoms, both showing a Jahn-Teller distortion. Whereas CuI exhibits a rare compressed coordination sphere with shorter axial Cu–N-bonds compared to the equatorial ones, the stretched coordination environment of Cu₂ is composed of longer axial and shorter equatorial Cu–N-bonds. In contrast, the copper(II) centers in complex **6** show no distortion at all, possessing six Cu–N-bond lengths of almost the same distance.

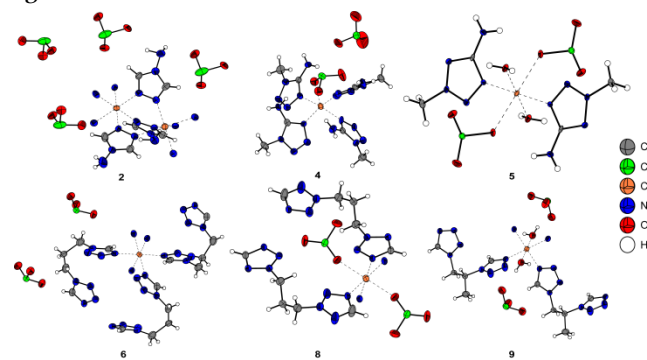


Figure 2. Different coordination modes of copper(II) chlorate complexes [Cu₂(4-ATRI)₆](ClO₃)₄ (**2**), [CuClO₃(1-MAT)₄ClO₃] (**4**), [Cu(ClO₃)₂(H₂O)₂(2-MAT)₂] (**5**), [Cu(1,1-dtp)₃](ClO₃)₂ (**6**), [Cu(ClO₃)₂(2,2-dtp)₂] (**8**) and [Cu(H₂O)₂(i-dtp)₂](ClO₃)₂ (**9**) determined by low temperature X-ray diffraction. Ellipsoids are drawn at the 50% probability level.¹²

For the determination of the compounds' deflagration to detonation transition (DDT) capability the hot plate test, hot needle test and plate dent test (Figure 3) were performed. The most promising compounds in terms of performance and thermal stability are complexes **2** and **8**. Their physicochemical properties are summarized in Table 1 and compared with that of lead azide. The sensitivities toward mechanical stimuli are comparable to those observed for Pb(N₃)₂, whereas the susceptibility against electrostatic discharge is lower, making them safer to handle. The compounds possess both good densities and thermal stabilities.

Copper(II) chlorate complexes **2** and **8** were tested in copper shell initiation tests and showed positive DDTs toward the secondary explosive PETN (Figure 3 A and 3B). In the laser ignition tests (Figure 1C) all complexes, except di-aqua compound **9**, showed a detonation differing in the required energy input between 0.17–25.5 mJ. However, UV-Vis measurements showed that the complexes only exhibit moderate absorption in the laser wavelength area (Figure 3C). Complex **2** cannot be compared with its perchlorate analogue since no energetic properties were explored.¹³ Comparing **8** with the corresponding perchlorate complex

(4-ATRI as ligand) shows a higher decomposition temperature (250 °C), while possessing a significantly lower density (ca. 1.4 g cm⁻³). It also shows a higher friction sensitivity (8.8 N) and was positive in PETN initiation tests.¹⁴

Table 1. Physicochemical properties of compound 2 and 8 compared to lead azide^[15].

	2	8	Pb(N₃)₂¹⁵
Formula	C ₁₂ H ₂₄ Cl ₄ Cu ₂ N ₂₄ O ₁₂	C ₁₀ H ₁₆ Cl ₂ CuN ₁₆ O ₆	PbN ₆
FW [g mol ⁻¹]	965.37	590.79	291.24
ρ_{calc} [g cm ⁻³]	1.964 (143)	1.821 (173)	4.8
(T [K])			
IS [J] ^{a)}	1	1	2.5–4
FS [N] ^{b)}	< 5	< 5	0.1–1
ESD [m] ^{c)}	15	50	6–12
T _{dec} [°C] ^{d)}	186	176	320–360

a) impact sensitivity according to the BAM drophammer (method 1 of 6). b) friction sensitivity according to the BAM friction tester (method 1 of 6). c) electrostatic discharge sensitivity (OZM ESD tester). d) temperature of decomposition indicated by exothermic event according to DTA (onset temperatures at a heating rate of 5 °C min⁻¹).

The toxicity measurements, using luminescent marine bacterium *Vibrio fischeri* NRRL-B-11177, for compound 3 and comparison with the corresponding copper(II) perchlorate complex – recently published by our group¹⁶ – prove the lower toxicity toward aquatic life of chlorate compounds.

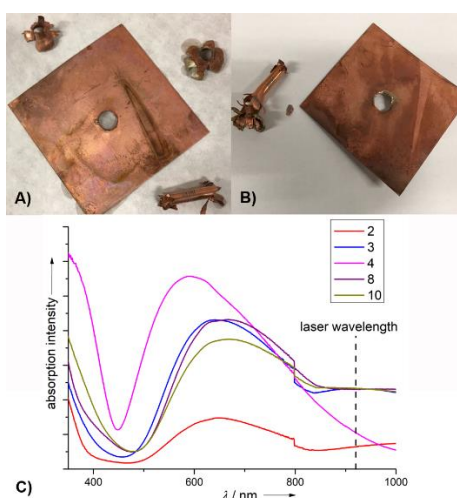


Figure 3. positive PETN initiation test of compound 2 A) and 8 B); C): solid-state UV-Vis measurements which were correlated to the laser initiation experiments.

In conclusion, we demonstrated a straightforward and low-cost synthetic route toward energetic copper(II) chlorate complexes. Complexation of Cu(ClO₃)₂ assures stabilization and tuning of the energetic character by the simple selection of different nitrogen-rich ligands based on tri- and tetrazole derivatives. In the course of this work, ten new coordination compounds were successfully synthesized and comprehensively compared with each other. All ten ligands lead to a disappearance of the high hygroscopy of pure copper(II) chlorate. For the first time, X-ray crystal structures of all compounds were determined and the previously predicted structure of 2^{8c} successfully proven. Thermal stability measurements by DTA showed exothermic decomposition temperatures above 150 °C for most of the compounds. Easy ignition by heat was proven by the hot needle and hot plate tests. In addition, the most promising primary explosives 2 and 8 showed excellent initiation capabilities toward the secondary PETN indicated by positive deflagration to detonation transitions. The use of alkyl-bridged ditetrazoles with longer chain lengths leads to an improvement of the mechanical sensitivities while maintaining a highly energetic character. This could be a promising concept for desensitization of energetic (copper(II) chlorate) complexes in the future. Toxicity measurements using *vibrio fischeri* of compound 3 showed a lower toxicity in comparison to the analogous perchlorate complex and confirmed the higher environmental friendliness of chlorate compounds. During the laser ignition experiments detonation of almost every compound was observed and demonstrated the great suitability of chlorate complexes in future laser initiation systems.

ASSOCIATED CONTENT

Supporting Information. 1. Experimental Procedure and General Methods; 2. Results and Discussion; 2.1 Synthesis; 2.2 Crystal Structures; 2.3 Sensitivities and Thermal Stability, 2.4 Laser Ignition Tests, 2.5 UV-Vis Spectroscopy, 2.6 Initiation Capability Tests, 2.7 Toxicity, 2.8 X-Ray Diffraction, 2.9 IR Spectroscopy; 3. References.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡These authors contributed equally.

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- (12) Selected X-ray data: **2**: C2/m, a 13.5622(16) Å, b 15.5713(18) Å, c 7.7338(15) Å, β 91.559(12)°, V 1632.6(4) Å³, Z 4, ρ 1.964 g cm⁻³; **4**: P2₁/n, a 13.1028(10) Å, b 10.7288(8) Å, c 16.2265(14) Å, β 95.036(7)°, V 2272.3(3) Å³, Z 4, ρ 1.832 g cm⁻³; **5**: P-1, a 6.5617(3) Å, b 7.5260(4) Å, c 9.0097(4) Å, α 111.762(2)°, β 98.711(2)°, γ 104.197(2)°, V 385.81(3) Å³, Z 1, ρ 2.000 g cm⁻³; **6**: P-3c1, a 10.9642(2) Å, c 14.3772(4) Å, V 1496.78(8) Å³, Z 2, ρ 1.711 g cm⁻³; **8**: C2/c, a 14.6638(7) Å, b 8.9883(5) Å, c 16.3538(8) Å, β 90.324(5)°, V 2155.44(19) Å³, Z 4, ρ 1.821 g cm⁻³; **9**: C2/c, a 15.0672(5) Å, b 9.0113(3) Å, c 17.5426(6) Å, β 97.696(3)°, V 2360.39(14) Å³, Z 4, ρ 1.764 g cm⁻³.
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