

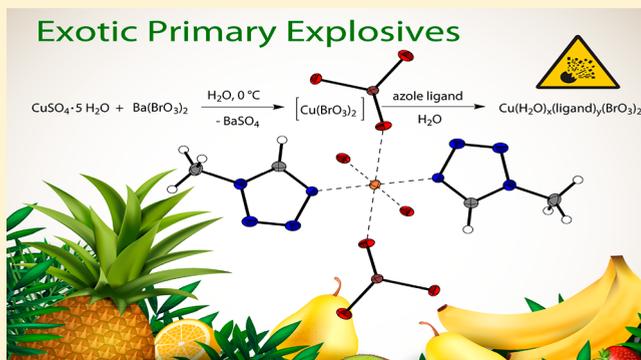
Nitrogen-Rich Copper(II) Bromate Complexes: an Exotic Class of Primary Explosives[†]

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S Supporting Information

ABSTRACT: Because of the ongoing very challenging search for potential replacements of the currently used toxic lead-based primary explosives, new synthetic strategies have to be developed. In particular, the smart concept of energetic coordination compounds (ECC) has proven to hold great potential to solve this difficult and complex problem. The herein-described approach combines the exotic and neglected class of copper(II) bromate ECC with different environmentally friendly nitrogen-rich heterocycles, which exhibit the energetic properties of powerful primary explosives. The concept is the simple adjustment of the energetic properties of the complexes through alteration of the corresponding azoles. Six new copper(II) bromate complexes with reasonable sensitivities are featured in this study, which were synthesized in a practical and straightforward fashion, assured through easy access to copper(II) bromate obtained by metathesis reaction. Obtained compounds were comprehensively characterized through various analytical methods such as low-temperature X-ray diffraction, IR spectroscopy, and elemental analysis. Their sensitivities toward impact and friction were assessed through BAM standard techniques, together with their sensitivity against electrostatic discharge. Evaluation of the energetic properties of the newly synthesized compounds included examination of the respective thermal stabilities by differential thermal analysis. Furthermore, the complexes were tested regarding their behavior toward laser irradiation. Additionally, to receive insight into a possible correlation between the laser-investigated compounds' optical absorption and their ability to ignite by exposure to laser irradiation, UV–vis–near-IR spectra were recorded.



1. INTRODUCTION

Energetic materials include a wide range of chemical compounds and can be classified into four main subgroups: primary explosives, secondary explosives, pyrotechnics, and propellants.¹ In contrast to the high-performing secondary explosives, primaries embody compounds showing a very fast deflagration-to-detonation transition (DDT) after being initiated by a nonexplosive simple initiation impulse.^{1,2} The most commonly used primary explosives nowadays are lead styphnate (LS) and lead azide (LA), two compounds that possess highly toxic potential toward human and nature.^{3,4} To avoid exposure of toxic chemicals during the utilization and manufacturing of lead-containing primaries, modern research in the field of primary explosives focuses on the synthesis of new green compounds while maintaining the desired properties of LS and LA (Chart 1).^{5–10}

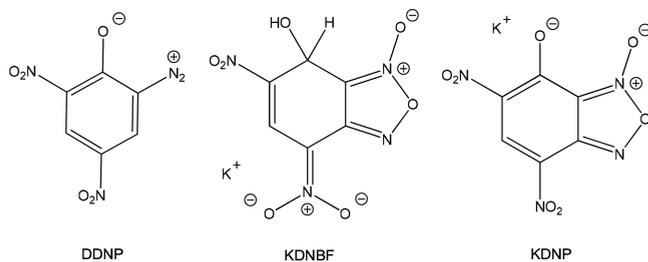
From all energetic characteristics, the previously discussed sensitivities are of high importance as well as high decomposition temperature and chemical and physical stability during long-term storage.² Moreover, to enable the substitution of commonly used compounds, the required synthesis of a new primary explosive should include as few as possible reaction steps and ought to be compatible with conventional materials (detonators, secondaries, and blasting caps).²

One promising approach to obtaining green primary explosives includes the synthesis of energetic coordination compounds (ECC), a strategy that has gained increased attention in recent years.^{7,17–20} Regarding the numerous parameters (metal center, ligand system, and counterion) that can be modified, the specific properties of a desired compound can be tailored incrementally toward the final target. In that manner, copper(II) bears great potential considering previous investigations,^{19,21} and, therefore, was examined extensively in combination with bromate as the anion in the course of this work. Besides the tedious search for possible replacements of LS and LA, recently, the research on primary explosives focused on laser-ignitable compounds.²² In contrast to the conventional methods of initiation through impact, friction, and electrostatic discharge, this new initiation method bears encouraging potential because of the circumstance that examined compounds do not require high sensitivities toward the customary stimuli.²³ Consequently, laser-ignitable energetic materials with high performance, high thermal stability, and an uncritical impact on the environment can be used as insensitive but powerful charges to allow much safer handling

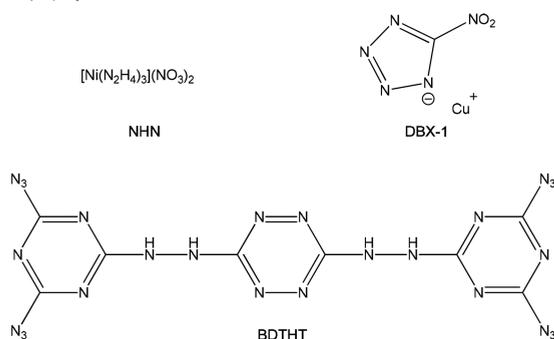
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Chart 1. Molecular Structures of Possible LS and LA Replacements^a

lead styphnate (LS) replacements:



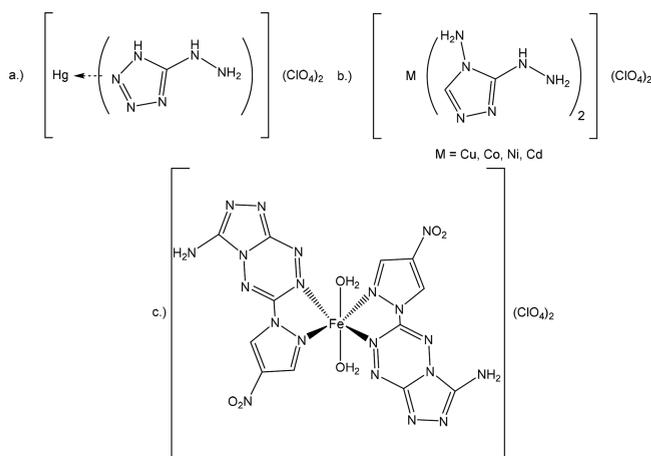
lead azide (LA) replacements:



^aDDNP = diazoniumdinitrophenolate,¹¹ KDNBF = potassium dinitrobenzofuroxan,¹² KDNP = 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide,¹³ NHN = nickel(II) hydrazine nitrate,¹⁴ DBX-1 = copper(I) nitrotetrazolate,¹⁵ and BDTH = 3,6-bis(2-(4,6-diazo-1,3,5-triazin-2-yl)hydrazinyl)-1,2,4,5-tetrazine.¹⁶

and to prevent undesired initiations.²² On the basis of the idea of primary explosives in the form of coordination compounds, Zhilin et al. isolated several very promising complexes in the early 2000s (Chart 2a,b), including the well-known *cis*-bis(5-nitro-2*H*-tetrazolato-*N*2)cobalt(III) perchlorate and 5-hydrazino-1*H*-tetrazolemercury(II) perchlorate.^{24–27} On the basis of these promising results, several research groups were starting

Chart 2. Different Laser-Ignitable Coordination Compounds^a



^a(a) 5-Hydrazino-1*H*-tetrazolemercury(II) perchlorate,²⁶ (b) 3-hydrazino-4-amino-1,2,4-triazole-based metal(II) perchlorates,²⁷ or (c) [(H₂N)TriTz^{NO₂}Pyr]₂Fe(H₂O)₂](ClO₄)₂.³¹

to examine laser-sensitive ECC for future applications in military and civil areas.^{28–30}

Bromates, particularly in the form of alkali salts, can be found in many different industrial processes (food production, synthetic reagents, dyeing, cosmetics, etc.) and are therefore an integral part of our daily life. While the use of alkali bromates (NaBrO₃ and KBrO₃) is rather common, the investigation of transition-metal bromates is relatively poor, especially with copper(II). Their high thermal stabilities,³² exceptional performances, and relatively low prices make alkali bromates promising candidates in explosive mixtures. The latter fact led to the development of manageable potassium bromate containing concrete cracking agents and airbag-gas-generating compositions, as well as the invention of detectors for bromate-containing explosive mixtures.^{33–35} Because of the strong oxidizing power of bromates and their high redox reactivity, mixtures with fuels or reducing agents have to be handled with great care. In particular, compositions with sulfur or organic compounds, such as dinitrotoluene or malonic acid, are highly unstable and tend to self-ignite within hours.³⁶

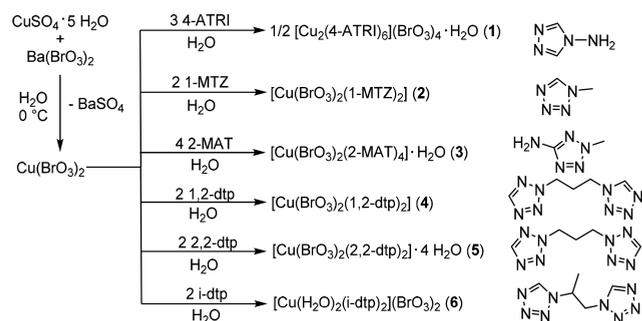
Only a very few copper(II) complexes [including complexes with ammonia, primary amines, 4-amino-1,2,4-triazole (4-ATRI)] using bromate as the counteranion are known in the literature so far.^{37,38} However, none of them was investigated for its crystal structure or has been described in relation to energetic materials. One of the very few, literature-reported examples uses the compound as a source for in situ generated Cu^IBr and as an alternative oxidizer (BrO₃[−] vs ClO₄[−]) in blue-light-emitting pyrotechnics.³⁹ The current contribution covers, as a further development of our recently published copper(II) chlorate complexes, analogous bromate-containing compounds with sensitivities in the range of primary explosives.⁴⁰ Obtained exceptional copper(II) bromate coordination compounds could be initiated by laser irradiation and their energetic character precisely tailored through the application of different nitrogen-donating azole-based ligands.

2. RESULTS AND DISCUSSION

2.1. Synthesis. Copper(II) bromate is poorly accessible, not commercially available, and exists with variable water contents (2–6 H₂O).^{41,42} Therefore, the driving force of barium sulfate precipitation was utilized to synthesize copper(II) bromate stoichiometrically in situ as an intermediate for further reaction with the ligands (Scheme 1) through metathesis of copper(II) sulfate and barium bromate. All ligands used were commercially available or were synthesized according to the literature. Because of the very good solubility of the used nitrogen-rich azoles and copper(II) bromate, a minimum amount of water was chosen as the reaction medium for the synthesis of ECC 1–6. As a result, the compounds often contain crystal water or aqua ligands. All attempts to change the reaction media to organic solvents led to decomposition of bromate to bromide because of its high redox activity [redox potential of E⁰ = 1.45 V (to BrO[−]); pH = 0], which is even slightly higher than that of perchlorate or chlorate [E⁰ = 1.43 V (to ClO[−])].⁴³

Most of the compounds were received in decent yields (57–85%) directly from the mother liquor in the form of single crystals suitable for X-ray diffraction. Only the compound [Cu₂(4-ATRI)₆](BrO₃)₄·H₂O (1) was isolated as a light-blue powder, and crystal growth was achieved through layering and very slow formation at the phase boundary.

Scheme 1. Synthesis of Complexes 1–6 Starting from Copper(II) Sulfate and Barium Bromate^a



^aOverview of the nitrogen-rich ligands used: 4-ATRI = 4-amino-1,2,4-triazole; 1-MTZ = 1-methyltetrazole; 2-MAT = 2-methyl-5-amino-tetrazole; 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).

All coordination compounds were filtered off, washed with small amounts of cold water, and dried in air. The complexes can easily be distinguished by IR spectroscopy (Figures S1 and S2) because of the different coordination modes of the anions and the water molecules or through the absence of crystal water.

2.2. Crystal Structures. All complexes were characterized by low-temperature single-crystal X-ray diffraction. The crystal structures were uploaded to the CSD database⁴⁴ and can be obtained free of charge as CCDC 1836542 (1), 1836543 (2), 1836539 (3), 1836540 (4), 1836537 (5), 1836541 (6), 1836544 (7), 1836538 (8). The bond lengths and angles of the coordinating ligands in the analyzed complexes are in the typical range of the tetrazole and triazole ligands and nearly the same as in the noncoordinating ligands.^{45–47} The ligands are therefore not part of the discussion in any of the following coordination compounds. All copper(II) bromate complexes show octahedral coordination with a Jahn–Teller distortion along the axial coordination sphere. In general, copper(II) bromate complexes tend to crystallize with water as solvent molecules [1, [Cu(BrO₃)₂(2-MAT)₄·H₂O (3), and [Cu(BrO₃)₂(2,2-dtp)₂·4H₂O (5)] or in the form of aqua ligands {[Cu(H₂O)₂(i-dtp)₂](BrO₃)₂ (6) and [Cu(H₂O)₂(en)₂](BrO₃)₂ (7)}. Only the bridging bromato anions in compounds [Cu(BrO₃)₂(1-MTZ)₂] (2) and [Cu(BrO₃)₂(1,2-dtp)₂] (4) prevented the inclusion of aqua molecules.

The monohydrated complex 1 is the only one presented with copper(II) ions exclusively coordinated by nitrogen atoms. It crystallizes in the form of blue blocks in the monoclinic space group *C2/c* with four formula units per unit cell and a calculated density of 2.299 g cm⁻³ at 143 K. The molecular unit contains two different copper(II) cations (Figure 1), and each is octahedrally coordinated by six triazole ligands. Both central atoms show a Jahn–Teller distortion, whereas the axial Cu–N bonds of Cu1 are shorter compared with those of Cu2. Three ligands are bridging between the same two copper(II) atoms and form polymeric chains.

2 shows the highest density (2.491 g cm⁻³ at 143 K) of all bromate complexes and crystallizes in the form of blue plates in the monoclinic space group *P2₁/c* with two formula units per unit cell. The bromate anions in 2 are now coordinating to the transition-metal(II) center in comparison to compound 1

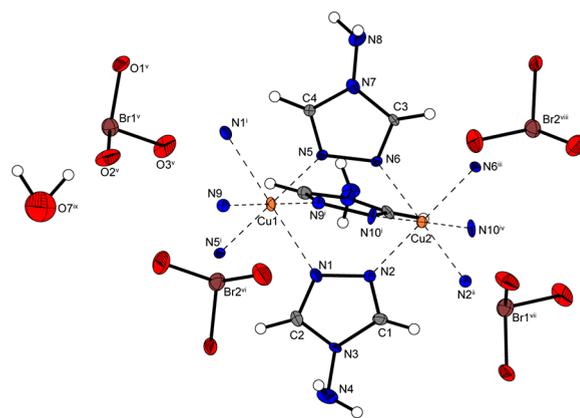


Figure 1. Copper(II) coordination environment of 1. Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected bond lengths (Å): Cu1–N1 2.298(6), Cu1–N5 2.052(6), Cu1–N9 2.022(7), Cu2–N2 2.019(6), Cu2–N6 2.036(6), Cu2–N10ⁱ 2.408(7). Selected bond angles (deg): N1–Cu1–N5 88.6(2), N1–Cu1–N9 88.8(2), N5–Cu1–N9 89.7(2), N2–Cu2–N6 91.4(2), N2–Cu2–N10ⁱ 89.7(2), N6–Cu2–N10ⁱ 88.0(2). Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, y, 1.5 - z$; (iii) $-x, y, 1.5 - z$; (iv) $x, -y, 0.5 + z$; (v) $-1.5 + x, 0.5 + y, z$; (vi) $0.5 - x, -0.5 - y, 1 - z$; (vii) $0.5 + x, -0.5 - y, 0.5 + z$; (viii) $0.5 - x, 0.5 + y, 1.5 - z$; (ix) $-1 + x, y, z$.

(Figure 2). Each of the bromato ligands is bridging between two different metal(II) atoms, building up polymeric 2D layers.

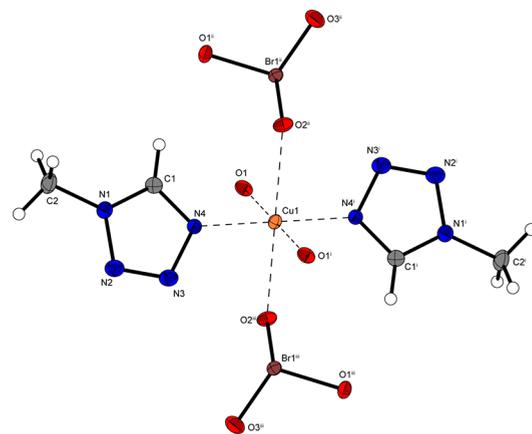


Figure 2. Copper(II) coordination environment of 2. Selected bond lengths (Å): Cu1–O1 2.009(2), Cu1–O2ⁱⁱ 2.346(2), Cu1–N4 1.987(3). Selected bond angles (deg): O1–Cu1–N4 90.71(10), O1–Cu1–O2ⁱⁱ 87.89(8), O2ⁱⁱ–Cu1–N4 89.80(9). Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $-x, 0.5 + y, 0.5 - z$; (iii) $x, 1.5 - y, -1.5 + z$.

The monodentate ligand 2-MAT leads to the formation of a closed octahedral coordination sphere in complex 3. It crystallizes in the form of green blocks in the monoclinic space group *P2₁/c* with four formula units per unit cell and exhibits the lowest density (1.983 g cm⁻³ at 143 K) of all compounds. The molecular unit consists of one copper(II) cation (Figure 3), coordinated by two bromato and four tetrazole ligands together with an additional crystal water molecule. In contrast to compound 2, the bromatos are only coordinating to one copper(II) central atom; therefore, the formation of polymeric structures does not occur. The water-free compound 4 crystallizes in the form of blue blocks in the monoclinic space group *P2₁/c* with two formula units per unit

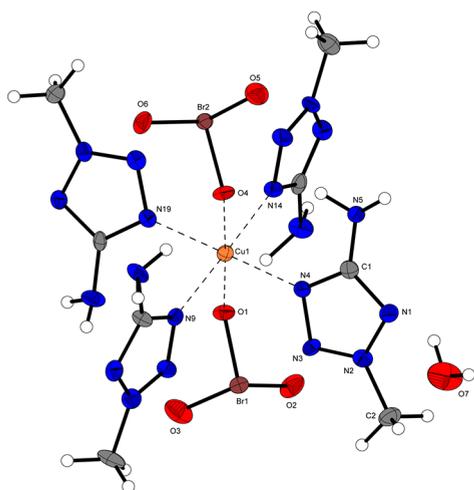


Figure 3. Molecular unit of **3**. Selected bond lengths (Å): Cu1–O1 2.367(4), Cu1–O4 2.381(4), Cu1–N4 2.018(5), Cu1–N9 2.057(5), Cu1–N14 2.043(5), Cu1–N19 2.033(5). Selected bond angles (deg): O1–Cu1–N9 88.57(17), O4–Cu1–N9 90.95(17), N4–Cu1–N9 91.08(19), N4–Cu1–N14 89.84(19).

cell and a calculated density of 2.142 g cm^{-3} at 130 K. The molecular unit is built up by one copper(II) cation (Figure 4),

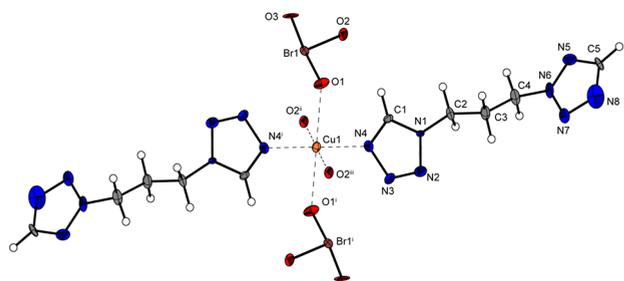


Figure 4. Copper(II) coordination environment of **4**. Selected bond lengths (Å): Cu1–O1 2.352(11), Cu1–O2ⁱⁱ 2.033(12), Cu1–N4 1.976(12). Selected bond angles (deg): O1–Cu1–N4 90.9(5), O1–Cu1–O2ⁱⁱ 96.2(4), O2ⁱⁱ–Cu1–N4 90.4(5). Symmetry codes: (i) $2 - x, -y, -z$; (ii) $x, -0.5 - y, -0.5 + z$; (iii) $2 - x, 0.5 + y, 0.5 - z$.

two coordinating ligands in equatorial positions, and two bridging bromato anions. The ditetrazole ligands are only connected with the 1-substituted tetrazole ring, while the 2-substituted ring is not coordinating at all. Similar to complex **2**, every bromato is bridging between two different copper(II) atoms, building up polymeric 2D layers.

5 crystallizes in the form of blue blocks in the triclinic space group $P\bar{1}$ with one formula unit per unit cell and a calculated density of 2.002 g cm^{-3} at 143 K. The molecular unit is composed of a copper(II) cation (Figure 5) with two coordinating bromato ligands in the axial positions, two 2,2-dtp ligands in the plane, and four noncoordinating crystal water molecules. In contrast to compounds **2** and **3**, the bromates are not bridging, but two neutral ligands are linking between two central metals, building up polymeric chains.

The diaqua coordination compound **6** crystallizes in the form of blue blocks in the monoclinic space group $C2/c$ with four formula units per unit cell and a calculated density of 1.989 g cm^{-3} at 143 K. In contrast to the other aqua complexes, the water molecules act as ligands whereas the bromate counterions are not coordinating. The molecular unit

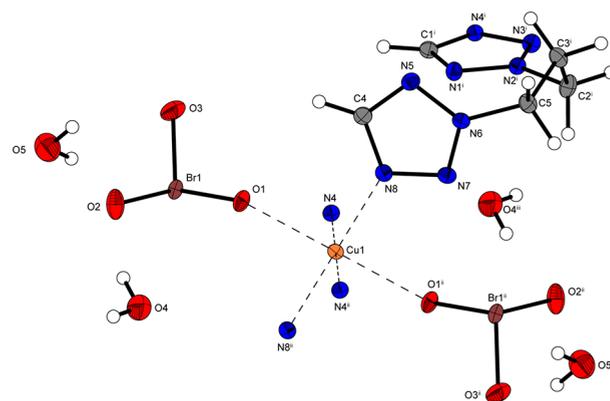


Figure 5. Copper(II) coordination environment of **5**. Selected bond lengths (Å): Cu1–O1 2.3200(13), Cu1–N4 2.0042(15), Cu1–N8 2.0335(15). Selected bond angles (deg): O1–Cu1–N4 93.85(5), O1–Cu1–N8 86.72(5), N4–Cu1–N8 91.38(6). Symmetry codes: (i) $3 - x, -y, 2 - z$; (ii) $2 - x, -y, 2 - z$; (iii) $1 - x, 1 - y, 2 - z$.

contains one central metal(II) (Figure 6) with two aqua ligands in axial positions, two equatorial ditetrazole molecules,

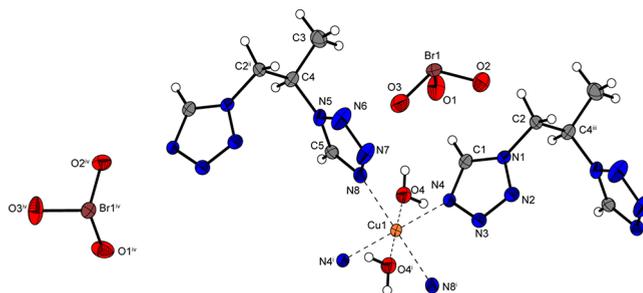
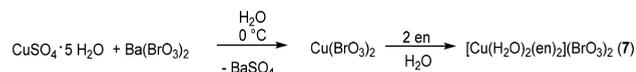


Figure 6. Copper(II) coordination environment of **6**. Selected bond lengths (Å): Cu1–O4 2.258(2), Cu1–N4 2.030(2), Cu1–N8 2.078(2). Selected bond angles (deg): O4–Cu1–N4 91.46(9), O4–Cu1–N8 85.56(9), N4–Cu1–N8 89.45(9). Symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $0.5 + x, -0.5 + y, z$; (iii) $-0.5 + x, 0.5 + y, z$; (iv) $0.5 + x, 0.5 - y, -0.5 + z$.

and two noncoordinating counterions. Analogously to complex **5**, the ligands are bridging between the copper(II) ions, building up polymeric chains.

Amiel described the synthesis of one of the first ever copper(II) bromate complexes with ethylenediamine (en) as the ligand in 1935 (Scheme 2). He suggested a monoclinic

Scheme 2. Synthesis of the Reinvestigated Complex **7**



space group for the obtained violet compound with a formula of $(\text{BrO}_3)_2\text{Cu}(\text{en})_2(\text{H}_2\text{O})$.³⁷ This compound was reinvestigated by single-crystal X-ray diffraction.

The reinvestigation of this compound (Figure 7) verifies indeed a monoclinic space group ($P2_1/c$) for compound **7**. Two chelating en molecules in the equatorial position and two aqua ligands in the axial position are building up closed octahedral coordination spheres around the copper(II) center with noncoordinating bromate counteranions in the molecular unit. The diaqua coordination compound crystallizes in the

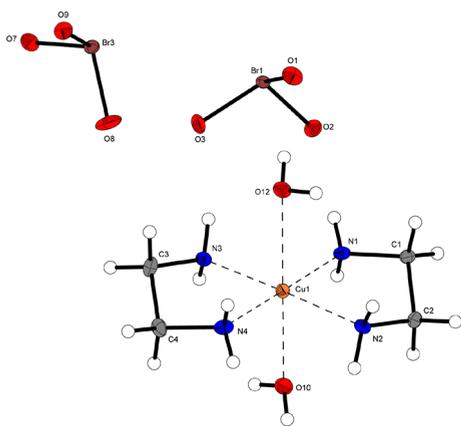


Figure 7. Molecular unit of 7. Selected bond lengths (Å): Cu1–N1 2.000(4), Cu1–N2 2.027(3), Cu1–N3 2.014(4), Cu1–N4 1.995(4), Cu1–O10 2.555(4), Cu1–O12 2.551(3). Selected bond angles (deg): N1–Cu1–N2 84.82(16), N1–Cu1–N3 94.90(16), N1–Cu1–N4 179.17(17), N1–Cu2–O10 83.98(15), N1–Cu2–O12 92.00(15).

form of purple blocks with six formula units per unit cell and a calculated density of 2.201 g cm^{-3} at 143 K.

The ligands highly influence the coordination mode of the bromate counterions. This affinity can also be observed in the various hydrates of copper(II) bromate. In $[\text{Cu}(\text{BrO}_3)_2(\text{H}_2\text{O})_2]$, the coordination sphere around the metal(II) center is built up of four bridging bromato and two aqua ligands.⁴¹ Blackburn et al. published the crystal structure of $[\text{Cu}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$ with noncoordinating anions, and the up-to-now unknown structure of $[\text{Cu}(\text{BrO}_3)_2(\text{H}_2\text{O})_4]$ (**8**), measured in the course of this work, shows coordination but no linking of the bromato ligands.⁴² The tetraaqua form of copper(II) bromate (**8**) crystallizes in the form of blue blocks in the orthorhombic space group *Pbca* with four formula units per unit cell and a calculated density of 2.975 g cm^{-3} at 143 K. Similar to complexes **3** and **5**, the coordination sphere around the copper(II) atom contains nonbridging bromato ligands in the axial positions and four extra equatorial aqua ligands (Figure 8).

2.3. Sensitivities and Thermal Stability. For the investigation of endothermic events, like dehydration or melting, and for determination of the thermal stabilities, differential thermal analysis (DTA) measurements with a

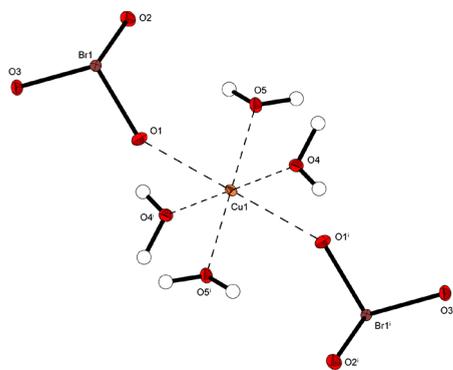


Figure 8. Molecular unit of 8. Selected bond lengths (Å): Cu1–O1 2.399(2), Cu1–O4 1.9572(19), Cu1–O5 1.9520(19). Selected bond angles (deg): O1–Cu1–O4 88.94(7), O1–Cu1–O5 95.11(7), O4–Cu1–O5 89.07(8). Symmetry code: (i) $1 - x, -y, 1 - z$.

heating rate of $\beta = 5 \text{ }^\circ\text{C min}^{-1}$ were performed. The sensitivities of the complexes toward electric discharge as well as against impact and friction have been determined according to BAM standards, and all compounds were classified in accordance with the U.N. recommendations on the transport of dangerous goods.⁴⁸ An overview of the physicochemical properties of all compounds is given in Table 1. The sensitivities toward mechanical stress are comparable to those for LS and LA, whereas the susceptibility against electrostatic discharge sensitivity (ESD) is lower, making them more secure.⁴⁹

The only endothermic occasions occurred during heating of coordination compounds **5** and **6** (Figure 9C) were the loss of their crystal water (**5**) or aqua (**6**) ligands at 103 and 129 $^\circ\text{C}$, respectively. The loss of crystal water molecules after heating in compounds **1** and **3** leads to instability of the whole molecule and results therefore in exothermic decomposition. One possible explanation of the higher thermal stability of compounds **5** and **6** could be the formation of water-free species that decompose at a later stage. Nevertheless, stable water-free products of **5** and **6** could not be obtained through dehydration. All ECCs have an exothermic decomposition temperature above 130 $^\circ\text{C}$, except complex **3**, which possesses a very low thermal stability of 92 $^\circ\text{C}$ due to the loss of crystal water. The highest temperature stability (169 $^\circ\text{C}$) shows the water-free 2D polymer **2**. The general trend becoming apparent is that bridging bromatos lead to crystallization of anhydrous complexes with higher thermal stabilities. Determination of the compounds' DDT capability by hot-plate and hot-needle testing (Figure 9A,B) was performed. Hot-needle tests were conducted by fixation of the sample underneath adhesive tape on a copper plate, followed by penetration with a red-heated needle. A compound's detonation typically indicates a valuable primary explosive, whereas the safe and practicable hot-plate test shows the performance of the unconfined sample toward fast heating on a copper plate. It does not necessarily allow any conclusions on a compound's capability as a primary explosive. All compounds, except complex **1**, showed deflagration in both tests. While the water-free compound **2** shows relatively high-temperature stability and only weak DDT, it is the other way around with compound **1**, possessing a great DDT but a low decomposition temperature.

2.4. Laser Ignition Tests and UV–Vis Measurements.

The laser ignition tests were performed with a single-pulsed 45 W InGaAs laser diode in the single-pulsed mode. The diode was coupled directly to an optical fiber with a core diameter of 400 μm and a cladding diameter of 480 μm . The optical fiber was linked via a SMA-type connector directly to the laser and to a collimator. The collimator, in turn, was connected to an optical lens, which was stationed in its focal distance ($f = 29.9 \text{ mm}$) to the sample. The lens was shielded from the explosive with sapphire glass. Transparent polycarbonate percussion caps were filled with approximately 25 mg of the compound, pressed with a pressure force of 1 kN, and sealed by a UV-curing adhesive. The confined samples were irradiated at a wavelength of 915 nm, a varying current of 7–8 A, a voltage of 4 V, and a varying pulse length of 0.10–15 ms, which combined the results in an approximate energy output of 0.17–30 mJ. The results of the laser experiments, which are classified in decomposition, deflagration, or detonation according to the generated sound, are summarized in Table 2.

Table 1. Physicochemical Properties of Compounds 1–6 as Well as LS and LA⁵⁰

	IS [J] ^a	FS [N] ^b	ESD [mJ] ^c	T _{endo} [°C] ^d	T _{exo} [°C] ^e	grain size [μm]
1	2	<5	25		137	<100
2	1	<5	60		169	100–500
3	2	<5	90		92	100–500
4	<1	10	150		146	100–500
5	8	108	260	103	150	100–500
6	1	40	150	129	146	100–500
LS	2.5–5	1.5	0.02–1.0	115	275–280	
LA	2.5–4	0.1–1	6–12		320–360	

^aImpact sensitivity according to the BAM drophammer (method 1 of 6). ^bFriction sensitivity according to the BAM friction tester (method 1 of 6). ^cElectrostatic discharge sensitivity (OZM ESD tester). ^dEndothermic peak indicating dehydration or loss of aqua ligands according to DTA (onset temperatures at a heating rate of 5 °C min⁻¹). ^eExothermic peak indicating decomposition according to DTA (onset temperatures at a heating rate of 5 °C min⁻¹).

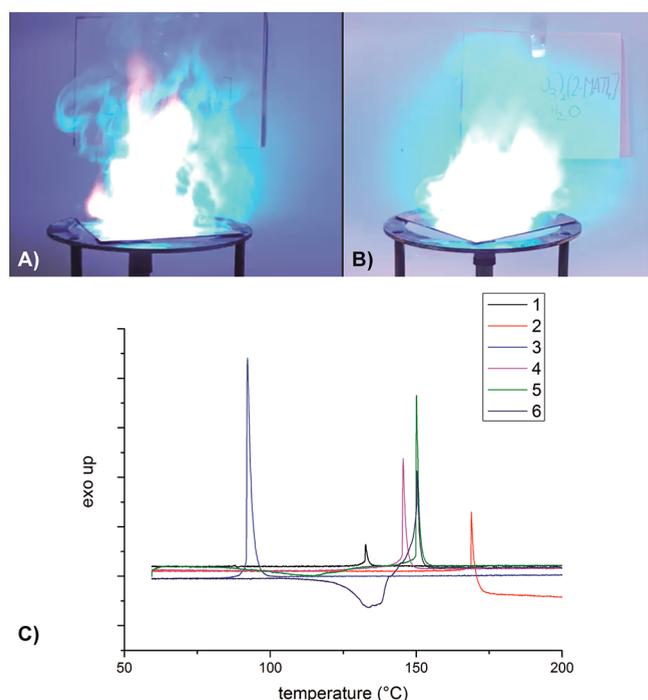


Figure 9. Hot-plate test of compounds 2 (A) and 3 (B). (C) DTA plots (5 °C min⁻¹) of complexes 1–6 shown in the range of 50–200 °C.

Table 2. Results of the Laser Ignition Tests of Compounds 1–6

	1	2	3	4	5	6
E _{max} [mJ]	0.17	30.0	0.20	0.17	5.10	2.55
outcome ^a	det.	det.	det.	det.	dec.	det.

^adet. = detonation; dec = decomposition. Operating parameters: current $I = 7\text{--}8$ A; voltage $U = 4$ V; theoretical maximal output power $P_{\text{max}} = 45$ W; wavelength $\lambda = 915$ nm; pulse length $\tau = 0.10\text{--}15$ ms.

All complexes, except tetraaqua compound 5, showed a detonation (Figure 10A,B) differing in the required energy input between 0.17 and 2.55 mJ. Compared to LA⁵¹ (3–30 mJ cm⁻²) and LS⁵² (1.3 J cm⁻²), the ignition of most of the ECCs is possible with lower energy input, although the results are difficult to compare because of their different setups. These results correlate with the observed sensitivities and make copper(II) bromate complexes promising compounds for laser ignition with low initiation energies.

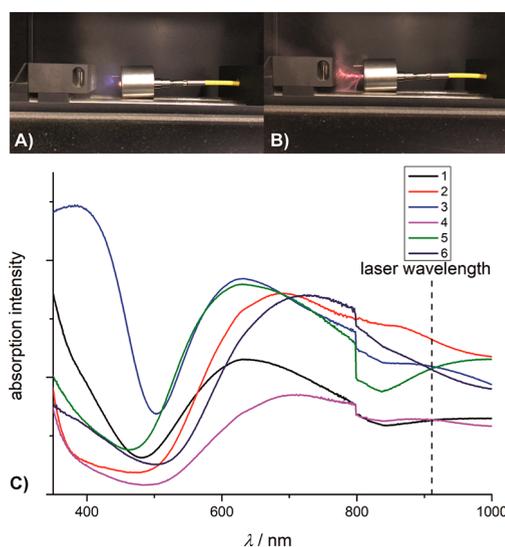


Figure 10. Positive laser initiation tests of compounds 2 (A) and 6 (B). (C) Solid-state UV–vis measurements that were correlated with the laser-initiation experiments.

In order to gain insight toward the laser-initiation mechanism, solid-state UV–vis measurements were performed in the range of 350–1000 nm for all complexes (Figure 10C). The step in the absorption intensity at 800 nm in the spectra is caused by a detector change. The UV–vis spectra exhibit only qualitative character.

Because of the characteristic d–d transitions, the spectra show absorptions in the UV, visible, and near-IR regions typical for copper(II) compounds. The mechanism for laser initiation is still not fully understood, and many pathways, such as electronic or thermal, are imaginable.⁵³ Because of the different coordination spheres, no conclusions can be drawn about the influence of the metal–ligand bond energy toward the color of the compounds. Compound 3, the only green copper(II) bromate complex, shows absorption maxima close to 400 and 600 nm. All other copper(II) bromate complexes show absorption maxima close to 350 and 600 nm with only minor deviations among each other. All complexes show only minor absorptions at the laser wavelength of 915 nm. The excitation at 915 nm could be a conceivable explanation for the initiation. The process of laser ignition probably depends on multiple parameters, and more investigations are necessary for a better understanding of the laser-initiation mechanism in the future.

2.5. Toxicity Determination and Mass Spectrometry (MS) of Decomposition Gases. The commercially available bioassay system LUMIStox test (luminescent marine bacterium *Vibrio fischeri* NRRL-B-11177), which measures the toxicity in aqueous media, is a valuable indicating device when it comes to groundwater contamination. The half-maximal effective concentration EC_{50} of these compounds was determined after an incubation time of 30 min (the toxicity level after 30 min of incubation: very toxic, $<0.10 \text{ g L}^{-1}$; toxic, $0.10\text{--}1.00 \text{ g L}^{-1}$; nontoxic, $>1.00 \text{ g L}^{-1}$).⁵⁴ With an EC_{50} (30 min) value of 0.21 g L^{-1} for compound **2**, it has to be considered as toxic, which is not surprising, because of the known toxicity of copper(II) compounds toward microorganisms.⁵⁵ Compared to the corresponding copper(II) chlorate and perchlorate complex, recently published by our group,^{56,40} with EC_{50} values of 0.19 and 0.13 g L^{-1} , respectively, the lower toxicity toward aquatic life of bromate compounds is proven.

For analysis of the gaseous decomposition products, a sample of approximately 40 mg of compound **2** was heated to $200 \text{ }^\circ\text{C}$ in a nitrogen gas flow and the formed gases were detected with a Cirrus3-XD quadrupole mass spectrometer (Figure 11). The spectra show the formation of oxygen (32), CO_2 (44), and small amounts of water (18). No formation of toxic Br_2 or HBr was observed.

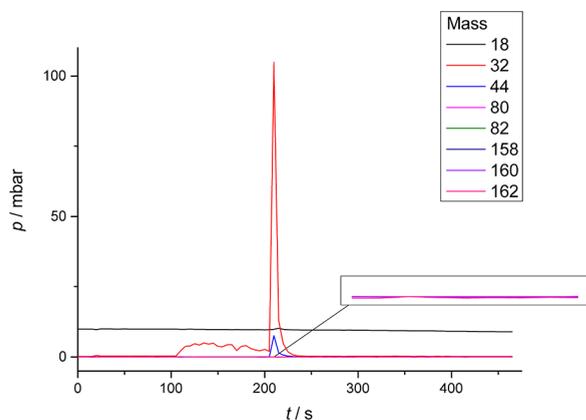


Figure 11. Results of the MS gas analysis of the decomposition products of compound **2**.

3. CONCLUSION

We demonstrated the next step in the development toward environmentally benign perchlorate-free ECCs with our exclusive concept of using bromate anions as “exotic” oxidizing species. The six newly synthesized and investigated copper(II) bromate compounds with azole ligands represent a considerable contribution to the coordination chemistry in general and in particular to ECC because of the enormous lack of literature regarding this topic. The displayed synthesis of the complexes is a straightforward and low-cost synthetic route toward modern lead-free primary explosives with promising performance characteristics. The simple complexation of $\text{Cu}(\text{BrO}_3)_2$ with different nitrogen-rich ligands based on tri- and tetrazole derivatives assures the formation of energetic compounds with high densities. The trend of inclusion of water into many of the structures can hardly be explained by the average oxophilicity of copper(II); however, it can be prevented by the formation of 2D polymeric layers caused by

bridging bromate ligands. X-ray studies of all compounds gave insight into the fascinating coordination variety of copper(II) bromate complexes highly depending on the ligands used. The compositions of complexes **1–6** were confirmed by elemental analysis and are in accordance with the crystal structures observed. In addition, the X-ray structure of the up-to-now unknown tetrahydrate of copper(II) bromate **8** could successfully be determined and the previously predicted structures of **1**³⁸ and **7**³⁷ proven wrong. Most of the compounds showed exothermic decomposition temperatures above $135 \text{ }^\circ\text{C}$ in thermal stability measurements by DTA. In comparison to the analogous perchlorate and chlorate complexes, ECC **2** showed a lower environmental hazardousness toward aquatic life in toxicity assessments using *V. fischeri*, which proves the higher environmental friendliness of bromate compounds. Within preliminary analysis of decomposition gases, no HBr and Br_2 formation was observed in the MS spectra. Detonations during laser-ignition experiments of nearly every single compound revealed the great capability of copper(II) bromate complexes in future laser-initiation systems.

4. EXPERIMENTAL SECTION

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros, and ABCR). ^1H and ^{13}C NMR spectra were recorded with neat solids as samples at ambient temperature using a JEOL Eclipse 270, JEOL EX 400, or JEOL Eclipse 400 instrument. The chemical shifts quoted in parts per million in the text refer to typical standards such as tetramethylsilane (^1H and ^{13}C). Dehydration, melting, and decomposition temperatures of the described compounds were measured through DTA with an OZM Research DTA 552-Ex instrument. The samples were measured in a range of $25\text{--}400 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. IR spectra were measured with pure samples on a PerkinElmer BXII FT-IR system with a Smith DuraSampler IR II diamond attenuated total reflectance instrument. Determination of the carbon, hydrogen, nitrogen, and sulfur contents was carried out by combustion analysis using an Elementar Vario El analyzer (the nitrogen values determined are often lower than the calculated ones because of their explosive behavior). UV-vis spectra were recorded in the solid state using a Varian Cary 500 spectrometer in the wavelength range of $350\text{--}1000 \text{ nm}$. Impact sensitivity tests were carried out according to STANAG 4489⁵⁷ modified instruction⁵⁸ using a BAM (Bundesanstalt für Materialforschung) drophammer.⁵⁹ Friction sensitivity tests were carried out according to STANAG 4487⁶⁰ modified instruction^{60,61} using the BAM friction tester. The classification of the tested compounds results from the “U.N. Recommendations on the Transport of Dangerous Goods”.⁶² Additionally, all compounds were tested for their sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.S7.⁶³ Liquid-dried luminescent bacteria of the strain *V. fischeri* NRRL-B-11177 provided by the HACH LANGE GmbH were used for the luminescent bacteria inhibition test to determine their toxicity toward aquatic organisms according to a modified procedure.⁶⁴ All of the obtained coordination compounds were washed with cold water, dried overnight in air, and used for analytics without further purification.

Caution! All investigated compounds are potentially explosive energetic materials, which show partly increased sensitivities toward various stimuli (e.g., elevated temperatures, impact, friction, or electrostatic discharge). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves, Kevlar sleeves, and ear plugs) have to be applied while synthesizing and handling the described compounds. Especially compound **1** must be handled with great care!

General Procedure for the Preparation of Complexes 1–7. Copper(II) sulfate pentahydrate (62.4 mg , 0.25 mmol) and barium bromate (98.3 mg , 0.25 mmol), each dissolved in 5 mL of water, were combined and stirred mechanically for 10 min, and the precipitated

barium sulfate was filtered off. The aqueous filtrate was dried under reduced pressure and the obtained copper(II) bromate dissolved in 2 mL of water. Stoichiometric amounts of the ligand dissolved in 1 mL of water were added under stirring. The reaction mixtures were left to crystallize, and the solids were filtered off, washed with cold water (2 mL), and dried in air. Only one single crystal of compound **7** was picked for X-ray determination experiments, and the complex was not further analyzed. The up-to-now unknown structure of **8** was picked out of a complex solution, which was left for crystallization as a single crystal, and a pure product for further investigation was not obtained.

$[Cu_2(4-ATRI)_6](BrO_3)_4 \cdot H_2O$ (**1**). Compound **1** was isolated as a light-blue precipitate. Yield: 116 mg (0.20 mmol, 80%). Single-crystal growth was achieved by overlaying an aqueous solution (8 mL) of copper(II) bromate with an ethanolic solution (8 mL) of 4-ATRI, separated by a mixture (4 mL) of water/ethanol (50/50). After 7 days, blue rods suitable for X-ray determination were obtained.

DTA (5 °C min⁻¹) onset: 137 °C (exothermic). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3545 (vw), 3250 (m), 3208 (w), 3153 (m), 3126 (m), 3089 (m), 3063 (m), 3018 (w), 2965 (w), 1644 (w), 1631 (w), 1553 (w), 1539 (w), 1491 (vw), 1424 (vw), 1396 (w), 1373 (w), 1321 (vw), 1222 (m), 1207 (w), 1095 (m), 1085 (m), 1050 (m), 1007 (w), 992 (w), 979 (w), 913 (w), 890 (w), 818 (s), 808 (s), 783 (vs), 761 (vs), 693 (w), 679 (w), 622 (vs). Elem anal. Calcd for C₁₂H₂₆Br₄Cu₂N₂₄O₁₃ (1161.29): C, 12.41; H, 2.26; N, 28.95. Found: C, 12.78; H, 2.28; N, 28.64. BAM drophammer = 2 J; friction tester = <5 N; ESD = 25 mJ (at grain size <100 μm).

$[Cu(BrO_3)_2(1-MTZ)_2]$ (**2**). Blue platelike crystals of complex **2** were obtained within 5 days and were suitable for X-ray determination. Yield: 89.4 mg (0.18 mmol, 73%).

DTA (5 °C min⁻¹) onset: 169 °C (exothermic). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3143 (m), 3034 (w), 1762 (vw), 1522 (m), 1472 (w), 1304 (w), 1202 (m), 1178 (vw), 1109 (m), 1066 (w), 1036 (w), 1003 (w), 883 (m), 862 (vs), 788 (s), 726 (s), 708 (s), 686 (vs), 652 (s). Elem anal. Calcd for C₄H₈Br₂CuN₈O₆ (487.51): C, 9.85; H, 1.65; N, 22.99. Found: C, 10.11; H, 1.81; N, 23.13. BAM drophammer = 1 J; friction tester = <5 N; ESD = 60 mJ (at grain size 100–500 μm).

$[Cu(BrO_3)_2(2-MAT)_4] \cdot H_2O$ (**3**). Green blocks suitable for X-ray determination of the monohydrated complex **3** crystallized within 3 days. Yield: 106 mg (0.14 mmol, 58%).

DTA (5 °C min⁻¹) onset: 92 °C (exothermic). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3359 (m), 3317 (m), 3306 (m), 3223 (m), 3174 (w), 3020 (w), 2962 (w), 1629 (m), 1606 (m), 1557 (s), 1439 (m), 1422 (m), 1383 (w), 1345 (w), 1333 (w), 1195 (m), 1132 (w), 1103 (w), 1075 (w), 1023 (w), 803 (vs), 760 (vs), 749 (vs), 680 (m), 670 (w), 631 (m), 571 (w). Elem anal. Calcd for C₈H₂₂Br₂CuN₂₀O₇ (733.75): C, 13.10; H, 3.02; N, 38.18. Found: C, 13.13; H, 2.95; N, 38.37. BAM drophammer = 2 J; friction tester = <5 N; ESD = 90.0 mJ (at grain size 100–500 μm).

$[Cu(BrO_3)_2(1,2-dtp)_2]$ (**4**). Blue blocklike crystals of the water-free compound **4** were isolated within 7 days and were suitable for X-ray determination. Yield: 96.9 mg (0.14 mmol, 57%).

DTA (5 °C min⁻¹) onset: 146 °C (exothermic). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3144 (m), 1764 (w), 1741 (m), 1571 (w), 1516 (m), 1466 (m), 1457 (m), 1446 (m), 1396 (w), 1381 (m), 1366 (m), 1301 (w), 1287 (m), 1198 (m), 1180 (m), 1141 (m), 1134 (m), 1108 (w), 1059 (w), 1031 (m), 1015 (m), 1008 (m), 886 (m), 860 (s), 786 (s), 751 (m), 727 (w), 713 (s), 700 (vs), 677 (m), 654 (s). Elem anal. Calcd for C₁₀H₁₆Br₂CuN₁₆O₆ (679.70): C, 17.67; H, 2.37; N, 32.97. Found: C, 17.20; H, 2.47; N, 32.51. BAM drophammer = <1 J; friction tester = 10 N; ESD = 150 mJ (at grain size 100–500 μm).

$[Cu(BrO_3)_2(2,2-dtp)_2] \cdot 4H_2O$ (**5**). The four-crystal water-containing complex **5** crystallized within 7 days in the form of blue blocks suitable for X-ray determination. Yield: 113 mg (0.15 mmol, 60%).

DTA (5 °C min⁻¹) onset: 103 °C (loss of water), 150 °C (exothermic). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3524 (w), 3441 (w), 3367 (w), 3151 (w), 3125 (w), 3014 (w), 2985 (vw), 2970 (vw), 2945 (vw), 1741 (vw), 1737 (vw), 1652 (vw), 1623 (w), 1608 (w), 1573 (vw), 1512 (w), 1488 (w), 1474 (w), 1464 (w), 1447 (w), 1438 (w), 1382 (w), 1373 (w), 1359 (w), 1322 (w), 1306 (w), 1285 (w), 1254 (vw), 1209 (w), 1199 (w), 1187 (w), 1172 (m), 1153 (m), 1137 (m), 1101

(m), 1086 (m), 1076 (w), 1059 (w), 1031 (m), 1021 (m), 1012 (w), 982 (w), 936 (w), 890 (vw), 861 (w). Elem anal. Calcd for C₁₀H₂₄Br₂CuN₁₆O₁₀ (751.76): C, 15.98; H, 3.22; N, 29.81. Found: C, 16.46; H, 3.36; N, 31.06. BAM drophammer = 8 J; friction tester = 108 N; ESD = 260 mJ (at grain size 100–500 μm).

$[Cu(H_2O)_2(i-dtp)_2](BrO_3)_2$ (**6**). Product **6** was received within 8 days in the form of blue blocks suitable for X-ray determination. Yield: 152 mg (0.21 mmol, 85%).

DTA (5 °C min⁻¹) onset: 129 °C (loss of water followed by decomposition). IR (ATR, cm⁻¹): $\tilde{\nu}$ 3357 (w), 3267 (w), 3151 (w), 3116 (w), 3016 (w), 2986 (w), 2945 (vw), 2776 (vw), 2661 (vw), 1741 (vw), 1652 (w), 1571 (vw), 1512 (w), 1489 (w), 1437 (m), 1391 (w), 1376 (w), 1360 (w), 1321 (vw), 1304 (w), 1287 (w), 1211 (w), 1187 (m), 1173 (m), 1160 (w), 1127 (w), 1100 (m), 1086 (m), 1039 (m), 1031 (w), 1011 (m), 990 (w), 916 (w), 891 (w), 840 (s), 782 (vs), 753 (s), 719 (w), 675 (m), 665 (m), 632 (m), 532 (vw). Elem anal. Calcd for C₁₀H₂₀Br₂CuN₁₆O₈ (715.73): C, 16.78; H, 2.82; N, 31.31. Found: C, 16.91; H, 2.92; N, 31.81. BAM drophammer = 1 J; friction tester = 40 N; ESD = 150 mJ (at grain size 100–500 μm).

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.inorgchem.8b01045](https://doi.org/10.1021/acs.inorgchem.8b01045).

X-ray diffraction and IR spectroscopy of **1–6** (PDF)

Accession Codes

CCDC 1836537–1836544 contain the supplementary crystallographic data for this paper. 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.

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Notes

The authors declare no competing financial interest.

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