

# The Lithium Salts of Bis(azolyl)borates as Strontium- and Chlorine-free Red Pyrotechnic Colorants

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*Dedicated to Prof. Dr. Manfred Scheer on the Occasion of his 65th Birthday*

**Abstract.** After concerns regarding the use of chlorinated material for pyrotechnic items had reinforced, the action of the U.S. Environmental Protection Agency on health concerns about strontium ushered in a new era in the production of red light. Lithium was shown to impart red color to a pyrotechnic flame, however only a very narrow selection of such formulations can be found in the literature. Dihydrobis(azolyl)borates are a well investigated, easily accessible class of materials which have been proven to be suitable as pyrotechnic coloring agents. With their high nitrogen contents such moieties should also meet the

requirements of a low combustion temperature and a reducing flame atmosphere for a lithium-based red-burning composition. This work evaluates the capability of the lithium salts of dihydrobis(pyrazol-1-yl)borate, dihydrobis(1,2,4-triazol-1-yl)borate, and dihydrobis(tetrazol-1-yl)borate to serve as red color imparters. The latter compounds were characterized by multinuclear NMR experiments, IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction and were investigated with respect to their thermal stabilities as well as sensitivities toward various ignition stimuli.

## Introduction

The findings that the perchlorate anion impedes the iodide uptake into the thyroid gland<sup>[1]</sup> and that organochlorine compounds combust to highly carcinogenic polychlorinated aromatics<sup>[2]</sup> were followed by a reduction of the advised strontium level in drinking water by the U.S. Environmental Protection Agency due to its impact on skeletal development.<sup>[3]</sup> These events have recently motivated pyrotechnicians to break with the long-standing tradition of generating the metastable red light-emitting species strontium(I) chloride in a pyrotechnic flame by mixing strontium nitrate with a metallic fuel, poly(vinyl chloride) and potassium perchlorate as an additional chlorine donor.<sup>[4]</sup>

Lithium is the only other element capable of producing a color close to the desired purplish red of strontium in a pyrotechnic composition as shown by Klapötke et al. with the example of dilithium 3,3'-diamino-4,4'-dinitramino-5,5'-bi-1,2,4-triazolate trihydrate (Li<sub>2</sub>ANAT).<sup>[5]</sup> The low health hazard posed by lithium is expressed by its application in the treatment of mental disorders.<sup>[6]</sup> As in the case of a lithium-containing pyrotechnic composition gaseous atomic lithium is the metastable red light-emitter to be formed during burn-down,<sup>[7]</sup>

special precautions have to be taken in order to achieve a satisfying color performance. In contrast to molecular strontium(I) chloride elemental lithium produces two distinct emission lines at 671 and 610 nm,<sup>[5]</sup> which are covered by any kind of continuum. When lithium reacts with water vapor in the flame to give gaseous lithium hydroxide<sup>[7]</sup> or when magnesium combusts to solid magnesium oxide, such a broad emission band occurs and a rather pinkish flame color is observed.<sup>[8,9]</sup> Furthermore, if the flame temperature exceeds a critical value, higher energetic transitions are favored and orange light is yielded.<sup>[8]</sup> In order to circumvent these problems, a fuel-rich atmosphere<sup>[7]</sup> and low flame temperatures<sup>[8]</sup> are suggested.

Dihydrobis(azolyl)borates have been intensively studied over the past 50 years,<sup>[10]</sup> are accessible by only one reaction step and have even been reported to be suitable coloring agents for green-burning pyrotechnic items.<sup>[10c]</sup> Such salts and Li<sub>2</sub>ANAT have in common that both have high nitrogen contents to create a reductive flame atmosphere and to cool the flame.<sup>[11]</sup> The formation of the metastable green light-emitting species boron dioxide<sup>[12]</sup> should require an excess of oxygen in the flame so that the red color impression provoked by a lithium dihydrobis(azolyl)borate is expected to be predominant. This article concentrates on lithium dihydrobis(pyrazol-1-yl)borate and its 1*H*-1,2,4-triazole and 1*H*-tetrazole analogues and evaluates their capability for use as red pyrotechnic colorants.

## Results and Discussion

### Syntheses

Dihydrobis(azolyl)borates are commonly accessed by the acid-base reaction of borohydride with the desired azole ligand.<sup>[10]</sup> Due to the instability of borohydrides toward hydrolysis all samples were prepared under an atmosphere of dry

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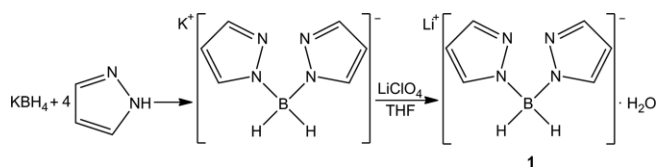
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201900132> or from the author.

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argon by means of standard Schlenk techniques and exclusively distilled solvent was used. The reactions proceed with the release of hydrogen so that pressure compensation has to be ensured, e.g. by adding a bubble counter.

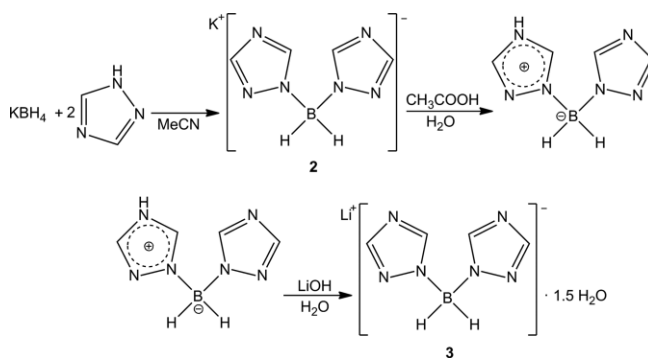
According to literature, potassium dihydrobis(pyrazol-1-yl)borate is accessible in a yield of 74% by melting four equivalents of 1*H*-pyrazole at 90 °C and subsequent reaction with one equivalent potassium borohydride at temperatures below 115 °C for 20 hours.<sup>[10a]</sup> The given temperature range is quite large so that different reaction temperatures were tested and the compositions of the crude products were investigated by <sup>1</sup>H-coupled <sup>11</sup>B NMR spectroscopy. When heating the reaction mixture to 110 °C, only minor amounts of borohydride and intermediate trihydro(pyrazol-1-yl)borate remained. Extending the reaction time by 20 hours significantly increased the yield (78%) even if the formation of higher substituted hydrotris(pyrazol-1-yl)borate was slightly enhanced (see Supporting Information). Potassium dihydrobis(pyrazol-1-yl)borate thus obtained was reacted with lithium perchlorate to give lithium dihydrobis(pyrazol-1-yl)borate monohydrate (**1**) (see Scheme 1). Nevertheless, this salt decomposes by 50% within four days.



**Scheme 1.** Synthetic route toward lithium dihydrobis(pyrazol-1-yl)borate monohydrate (**1**).

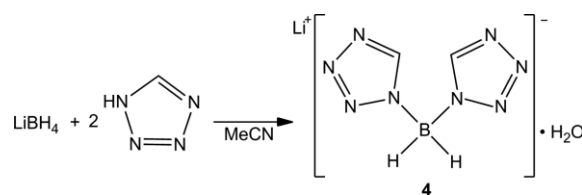
Since to the best of our knowledge no crystal structure has been reported for potassium dihydrobis(1,2,4-triazol-1-yl)borate (**2**) so far, the synthesis of this moiety was investigated further. The literature provides two synthetic approaches toward compound **2**: a melt reaction of potassium tetrahydroborate and two equivalents of 1*H*-1,2,4-triazole<sup>[10b]</sup> or refluxing a solution of these starting materials in acetonitrile for four days.<sup>[10c,10d]</sup> The latter method was chosen over the solvent-free alternative because 1*H*-1,2,4-triazole with its  $pK_a$  value of 10.0<sup>[13]</sup> is more acidic than pyrazole ( $pK_a = 20.4$ <sup>[14]</sup>) and thus higher volumes of hydrogen were expected to be released at once upon reaction with borohydride. However, the proposed reaction time of four days gave trihydro(1,2,4-triazol-1-yl)borate as the sole product. Elongation of the reaction time by two more days led to the target moiety the yield of which was successfully improved by doubling the concentrations of potassium tetrahydroborate and 1*H*-1,2,4-triazole (see Supporting Information). In the next step, potassium dihydrobis(1,2,4-triazol-1-yl)borate was reacted to the corresponding free acid with glacial acetic acid.<sup>[10c,d]</sup> The metathesis reaction of (1*H*-1,2,4-triazole)dihydro(1,2,4-triazol-1-yl)borane and lithium hydroxide was conducted to yield lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate (**3**) (see Scheme 2).

Potassium dihydrobis(tetrazol-1-yl)borate has also been shown to be viable by meltdown of potassium borohydride and



**Scheme 2.** Synthetic route toward lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate (**3**).

two equivalents of 1*H*-tetrazole or by heating a solution of these materials in *N,N*-dimethylacetamide at 100 °C for two hours.<sup>[10e]</sup> Here again the synthesis in solvent was preferred for testing its transferability to lithium dihydrobis(tetrazol-1-yl)borate since 1*H*-tetrazole is the most acidic azole in this row ( $pK_a = 4.9$ <sup>[13]</sup>). Additionally, compared to potassium the smaller lithium cation is a harder Lewis acid and should form a more reactive adduct with the soft Lewis base borohydride. Therefore, we considered a temperature of 80 °C to be sufficient for overcoming the activation energy barrier. This allowed us to replace dimethylacetamide by less toxic and easier removable acetonitrile (see Scheme 3). Lithium dihydrobis(tetrazol-1-yl)borate monohydrate (**4**) was formed under these reaction conditions but the presence of boric acid and tetrahydroxoborate in the crude product after washing with undistilled solvent suggests an incomplete conversion of the starting materials. Additionally, the deprotonation of 1*H*-tetrazole upon contact with moisture complicates the work-up and impedes the yield.



**Scheme 3.** Synthetic route toward lithium dihydrobis(tetrazol-1-yl)borate monohydrate (**4**).

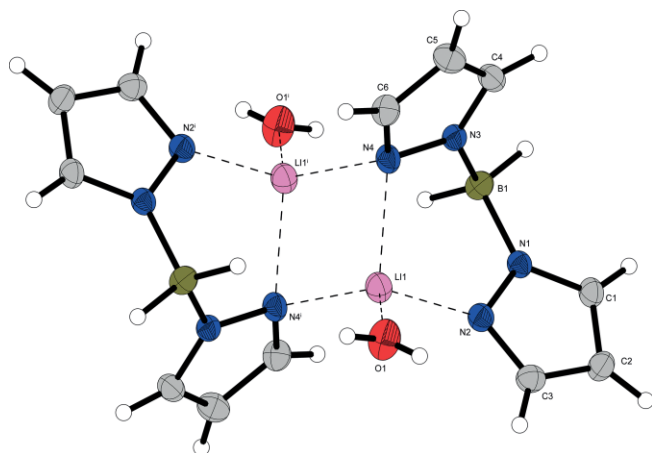
### Crystal Structures

Crystalline material of compound **3** was obtained directly from the mother liquor whereas crystals of **2** and **4** were grown from solutions in water or acetonitrile, respectively. Separation of compound **1** from impurities and mounting the crystals thus obtained in Kel-F oil even allowed for a crystal structure determination of this moiety before it further decomposed. Suitable single crystals were prepared and characterized by low-temperature X-ray diffraction.

Apart from **1** with the monoclinic space group  $P2_1/n$ , all of the salts crystallize in orthorhombic space groups (**2**:  $P2_12_12_1$ ; **3**:  $Pbcn$ ; **4**:  $Cmc2_1$ ).

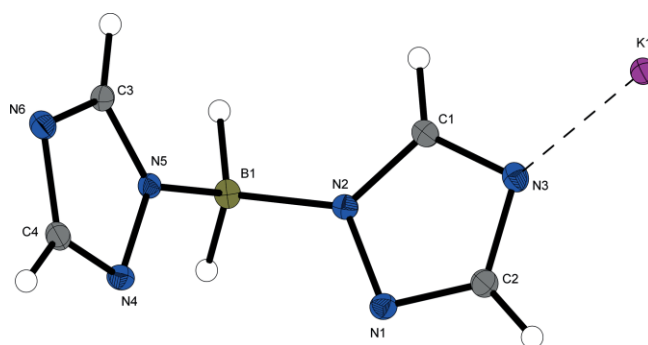
Considering that the density of the azoles inclines with increasing number of nitrogen atoms (*1H*-pyrazole:  $\rho = 1.03 \text{ g}\cdot\text{cm}^{-3}$  at 343 K;<sup>[15]</sup> *1H*-1,2,4-triazole:  $\rho = 1.39 \text{ g}\cdot\text{cm}^{-3}$  at 298 K;<sup>[16]</sup> *1H*-tetrazole:  $\rho = 1.53 \text{ g}\cdot\text{cm}^{-3}$  at 293 K<sup>[17]</sup>) this trend would also be expected for the respective lithium borates. The density of lithium dihydrobis(tetrazol-1-yl)borate monohydrate ( $\rho = 1.30 \text{ g}\cdot\text{cm}^{-3}$ ) exceeds that of lithium dihydrobis(pyrazol-1-yl)borate monohydrate ( $\rho = 1.28 \text{ g}\cdot\text{cm}^{-3}$ ) but the difference is rather small and lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate has the highest density ( $\rho = 1.40 \text{ g}\cdot\text{cm}^{-3}$ ). Even if moiety **4** forms a polymeric structure (see Figure 4) as opposed to the dimers observed for **1** (see Figure 1), the lithium cation in the latter is coordinated by two nitrogen atoms of one borate anion contributing to a closer packing. Compound **3** (see Figure 3) contains more crystal water, which fills the gaps, than the other two lithium salts.

In all of the three lithium salts, the cation has a distorted tetrahedral coordination sphere. In the case of **1** this coordination sphere consists of three nitrogen atoms of two neighboring borate anions and one aqua ligand, whereas in **3** and **4** lithium is coordinated by two nitrogen atoms of two borate anions and two water molecules. Interestingly, in moiety **1** two lithium cations are connected by the nitrogen atom N4 in a distorted square planar manner. In **3** two monomers share one aqua ligand so that the two lithium cations are angled to each other. Potassium dihydrobis(1,2,4-triazol-1-yl)borate appeared to be hygroscopic, possibly because it is the only among the investigated salts to crystallize without the inclusion of water (see Figure 1, Figure 2, Figure 3, and Figure 4).

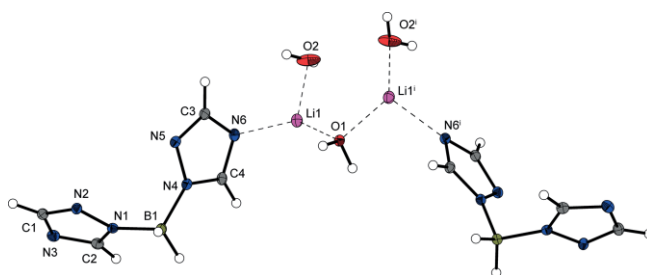


**Figure 1.** Dimer of  $\text{Li}[\text{H}_2\text{B}(\text{C}_3\text{H}_3\text{N}_2)_2]\cdot\text{H}_2\text{O}$  (**1**). Selected bond lengths /Å: B1–H1A 1.122(14), B1–H1B 1.138(14), N1–B1 1.5496(18), N3–B1 1.5547(18), N2–Li1 2.014(2), O1–Li1 1.928(2), N4<sup>i</sup>–Li1 2.086(2), N4–Li1 2.154(3); selected bond angles /°: N1–B1–N3 108.23(10), O1–Li1–N2 103.94(11), O1–Li1–N4<sup>i</sup> 114.99(12), N2–Li1–N4<sup>i</sup> 118.05(12), N2–Li1–N4 98.20(10), O1–Li1–N4 121.49(12), N4–Li1–N4<sup>i</sup> 99.89(10), Li1–N4–Li1<sup>i</sup> 80.11(9); symmetry code: (i) 1–x, –y, –z.

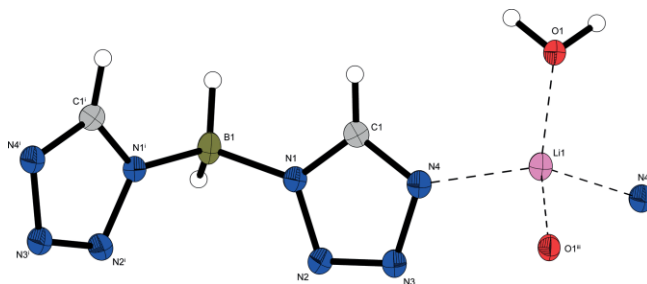
In general, the B–H and B–N distances as well as the N–B–N bond angles of compounds **1–4** are in the range of reported



**Figure 2.** Molecular unit of  $\text{K}[\text{H}_2\text{B}(\text{C}_2\text{H}_2\text{N}_3)_2]$  (**2**). Selected bond lengths /Å: B1–H1A 1.11(3), B1–H1B 1.16(2), N2–B1 1.550(3), N5–B1 1.554(3), K1–N3 2.821(2); selected bond angles /°: N2–B1–N5 109.5(2), K1–N3–C1 123.23(15), K1–N3–C2 117.98(16).



**Figure 3.** Dimer of  $\text{Li}[\text{H}_2\text{B}(\text{C}_2\text{H}_2\text{N}_3)_2]\cdot 1.5 \text{ H}_2\text{O}$  (**3**). Selected bond lengths /Å: B1–H1A 1.104(13), B1–H1B 1.120(13), N1–B1 1.5553(16), N4–B1 1.5613(16), N6–Li1 2.052(2), O1–Li1 1.975(2), O2–Li1 1.952(2); selected bond angles /°: N1–B1–N4 109.31(9), O2–Li1–N6 119.89(11), O1–Li1–N6 103.14(10), O1–Li1–O2 115.81(11), Li1–O1–Li1<sup>i</sup> 115.66(10); symmetry code: (i) 1–x, y, –0.5–z.



**Figure 4.** Advanced molecular unit of  $\text{Li}[\text{H}_2\text{B}(\text{CHN}_4)_2]\cdot\text{H}_2\text{O}$  (**4**). Selected bond lengths /Å: B1–H1A 1.09(3), B1–H1B 1.07(3), N1–B1 1.568(2), N4–Li1 2.058(3), O1–Li1 1.952(5), O1<sup>iii</sup>–Li1 1.994(5); selected bond angles /°: N1–B1–N1<sup>i</sup> 108.16(18), O1–Li1–N4 111.36(15), O1–Li1–O1<sup>iii</sup> 106.9(2), O1<sup>iii</sup>–Li1–N4 104.40(15), N4–Li1–N4<sup>ii</sup> 117.4(2); symmetry codes: (i) 1–x, y, z; (ii) 2–x, y, z; (iii) 2–x, 2–y, 0.5+z.

values for potassium dihydrobis(pyrazol-1-yl)borate<sup>[18]</sup> (B–N 1.561 Å; N–B–N 110.6°), barium dihydrobis(1,2,4-triazol-1-yl)borate trihydrate<sup>[10c]</sup> (B–N 1.543–1.559 Å) and potassium dihydrobis(tetrazol-1-yl)borate<sup>[10c]</sup> (B–H 1.09–1.10 Å, B–N 1.553–1.561 Å; N–B–N 109.1°). The B–H bond lengths decrease and the B–N bonds are elongated when replacing *1H*-pyrazole as the substituent by *1H*-1,2,4-triazole or *1H*-tetrazole, respectively. This is due to the increasing number of

nitrogen atoms in the ring pushing electron density to the boron atom.

### Physico-Chemical Properties

In order to evaluate the applicability of the stable lithium salts of dihydrobis(1,2,4-triazol-1-yl)borate and dihydrobis(tetrazol-1-yl)borate in pyrotechnic formulations, the oxygen balances of the latter salts were calculated and the thermal stabilities as well as the sensitivities toward various ignition stimuli were determined (see Table 1). The oxygen balance of a compound with formula  $C_aH_bN_cO_d$  and molecular mass  $M$  describes the excess or deficit of oxygen occurring during complete combustion to  $CO_2$ ,  $H_2O$  and  $N_2$  [see Equation (1)].<sup>[19]</sup>

$$\Omega(CO_2) = \frac{d - 2a - b/2}{M} \times 1600 \quad (1)$$

Lithium and boron are assumed to be converted to  $Li_2O$ <sup>[20]</sup> and  $B_2O_3$ <sup>[21]</sup>, respectively. As expected from the decrease of the carbon content at the expense of nitrogen, the oxygen balance increases from moiety **3** to **4**. However, both salts have negative oxygen balances so that they should serve as both coloring and reducing agents. Furthermore, compounds **3** and **4** have very high decomposition temperatures, which render them suitable for use as pyrotechnic colorants. Salt **3** is insensitive toward the tested ignition stimuli, whereas **4** is sensitive toward impact. Environmentally benign red-burning pyrotechnic compositions should not only be able to keep up with in-service items in terms of performance but also regarding their

sensitivity.<sup>[22]</sup> Thus, moiety **4** does not seem to be a potential substitute for strontium-based red coloring agents.

### Pyrotechnic Formulations

Among the investigated compounds, lithium dihydrobis(1,2,4-triazol-1-yl)borate is the most promising candidate for application in pyrotechnics. This is due to its high thermal stability [ $T_{dec}(onset) = 317$  °C] and insensitive character. Therefore, it was tested for the production of a desirable red signature by preparing a modified composition of a chlorine-free red formulation described by *Sabatini et al.*<sup>[11]</sup> For this purpose, strontium nitrate was replaced by its ammonium salt serving as oxidizer and compound **3** was employed as both coloring and reducing agent due to its negative oxygen balance. In order to reduce the flame temperature and to minimize incandescence, the content of **3** was raised at the expense of magnesium (see Table 2).

In contrast to the control formulation A, the test composition B shows a burning behavior similar to a strobe (see Figure 5) but the dominant wavelengths of the light flashes are clearly in the red region of the electromagnetic spectrum (see Table 3). The discontinuous burn of B is also evident from its unusually long burn time.

However, B has a decomposition temperature in the range of the reference and is less sensitive toward several environmental stimuli (see Table 4).

According to literature, the addition of nitrocellulose as burn rate modifier and gas generator to a strobe composition increases the flash frequency<sup>[9]</sup> until it exceeds the human eye

**Table 1.** Physico-chemical properties of lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate (**3**) and lithium dihydrobis(tetrazol-1-yl)borate monohydrate (**4**).

	$\Omega(CO_2)$ /% <sup>a)</sup>	$T_{dec}(onset)$ /°C <sup>b)</sup>	<i>g.s.</i> / $\mu\text{m}$ <sup>c)</sup>	<i>FS</i> /N <sup>d)</sup>	<i>IS</i> /J <sup>e)</sup>	<i>ESD</i> /J <sup>f)</sup>
<b>3</b>	-96.22	317	100–500	>360	>40	>1.5
<b>4</b>	-54.58	213	<100	>360	10	0.20

a) Oxygen balance with respect to formation of  $CO_2$ ,  $Li_2O$  and  $B_2O_3$ . b) Onset decomposition temperature observed as exothermic peak during differential thermal analysis using a heating rate of  $\beta = 5$  K·min<sup>-1</sup>. c) Grain size. d) Friction sensitivity. e) Impact sensitivity. f) Electrostatic discharge sensitivity.

**Table 2.** Composition of *Sabatini et al.*'s chlorine-free red formulation A<sup>[11]</sup> and a formulation containing lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate B.

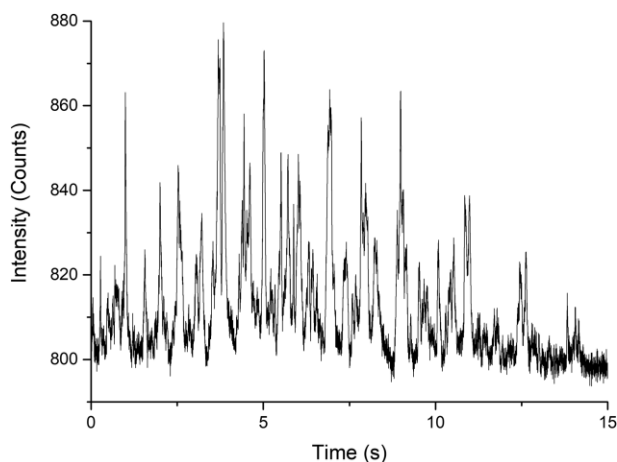
	$Sr(NO_3)_2$ /wt%	$NH_4NO_3$ /wt%	Mg 50/100 /wt% <sup>a)</sup>	$CH_3N_5$ /wt%	<b>3</b> /wt%	Epon 813 / Versamid 140 /wt% <sup>b)</sup>
A	48	–	33	12	–	7
B	–	48	12	–	33	7

a) Magnesium with a mesh size 50/100 (300  $\mu\text{m}$  > *g.s.* > 150  $\mu\text{m}$ ). b) Epon 813 and Versamid 140 in a weight percent-ratio of 4:1.

**Table 3.** Combustion parameters of formulations A and B.

	<i>BT</i> /s <sup>a)</sup>	$\lambda_d$ /nm <sup>b)</sup>	$\Sigma$ /% <sup>c)</sup>	<i>LI</i> /cd <sup>d)</sup>	<i>f</i> /Hz <sup>e)</sup>
A	3	608	72	32200	–
B	15	581–604	–	–	4

a) Burn time. b) Dominant wavelength. c) Spectral purity. d) Luminous intensity. e) Strobe frequency.



**Figure 5.** Strobe frequency spectrum of formulation B recorded using a wavelength range of 580.11–605.36 nm.

**Table 4.** Physico-chemical properties of formulations A and B.

	$T_{dec}(\text{onset}) / ^\circ\text{C}$ <sup>a)</sup>	$FS / \text{N}$ <sup>b)</sup>	$IS / \text{J}$ <sup>c)</sup>	$ESD / \text{J}$ <sup>d)</sup>
A	230	192	9	0.25
B	215	>360	20	0.75

a) Onset decomposition temperature observed as exothermic peak during differential thermal analysis using a heating rate of  $\beta = 5 \text{ K}\cdot\text{min}^{-1}$ . b) Friction sensitivity. c) Impact sensitivity. d) Electrostatic discharge sensitivity.

maximum sample rate of roughly 20 Hz<sup>[23]</sup> and a constant burning behavior is perceived. This approach might also lead to a continuously burning formulation employing salt 3.

## Conclusions

Three new lithium dihydrobis(azolyl)borate salts carrying 1*H*-pyrazole, 1*H*-1,2,4-triazole or 1*H*-tetrazole as ligands were synthesized in satisfactory yields via the Lewis acid-base reactions between borohydrides and the respective heterocycles. Lithium dihydrobis(pyrazol-1-yl)borate has a half-life as short as four days due to the basicity of 1*H*-pyrazole ( $\text{p}K_a = 20.4$ ) whereas the high acidity of 1*H*-tetrazole ( $\text{p}K_a = 4.9$ ) results in a highly exothermic character of the reaction with tetrahydroborate and reduced yields. No such problems were encountered in the case of lithium dihydrobis(1,2,4-triazol-1-yl)borate. These results suggest that the convenient preparation and sufficient stability of bis-substituted borates call for  $\text{p}K_a$  values of the heterocycles in the range of 1*H*-1,2,4-triazole. The lithium salts of dihydrobis(1,2,4-triazol-1-yl)borate and dihydrobis(tetrazol-1-yl)borate were characterized by IR spectroscopy, multinuclear NMR spectroscopy including  $^1\text{H}$ -coupled  $^{11}\text{B}$  NMR, elemental analysis, differential thermal analysis and sensitivity testing.

Furthermore, the crystal structures of all three compounds were elucidated by means of low-temperature single-crystal X-ray diffraction. Lithium dihydrobis(1,2,4-triazol-1-yl)borate proved to be thermally stable up to 317 °C and insensitive toward friction, impact and electrostatic discharge so that its

capability to produce a desirable red signature in a pyrotechnic formulation was determined. Red emissions by this salt were observed even if no constant burn could be achieved without further formulating. However, the strobe-like burning behavior might be tailored toward a continuous combustion in the future by adding nitrocellulose as both burn rate modifier and gas generator.

**Supporting Information** (see footnote on the first page of this article): The supporting information includes experimental methods, IR spectra, NMR spectra, X-ray data, DTA plots as well as detailed information on synthesis optimizations, ageing studies and burning tests.

## Acknowledgements

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 authors want to thank Prof. Konstantin Karaghiosoff, Christin Kirst, Maximilian H. H. Wurzenberger, and Maurus B. R. Völkl for their contributions to this work. Open access funding enabled and organized by Projekt DEAL.

**Keywords:** Lithium dihydrobis(azolyl)borates; Lewis acid-base reaction; Red pyrotechnic colorants; Strontium-free; Chlorine-free

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Received: June 24, 2019

Published Online: August 8, 2019