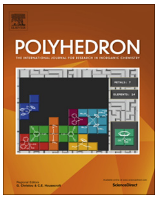
Polyhedron 157 (2019) 71–89

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Preparation and characterization of bis(guanidinium) and bis(aminotetrazolium)dodecahydroborate salts: Green high energy nitrogen and boron rich compounds

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ARTICLE INFO

Article history:
Received 24 July 2018
Accepted 19 September 2018
Available online 28 September 2018

Keywords:
Dodecahydroborate salts
High energy materials
Propellants
Green materials
Nitrogen rich cations

ABSTRACT

This paper describes the syntheses, crystallization, characterization and energetic properties (calorimetry) of *closo*-dodecahydroborate salts with guanidinium and aminotetrazolium based cations. The salts were readily produced in good yields by metathesis (ion exchange) reactions depending on the water solubility of the dodecahydroborate salts. Water insoluble salts can be synthesized from the potassium or sodium salts by a simple metathesis reaction with the corresponding halide of the desired organic cation. Water soluble salts can be prepared via two consecutive metathesis reactions: the halide is first converted to the corresponding sulfate, which is reacted in turn with barium dodecahydroborate, yielding the water soluble organic closo$(B_{12}H_{12})^{2-}$ salt and the insoluble $BaSO_4$. The product salt is conveniently isolated by water evaporation. The aminotetrazolium salt **12d** gives nice crystals when recrystallized from DMF and NMP but incorporate solvent. Guanidinium salt **15a** recrystallizes from nicely from water as a monohydrate. Thermogravimetric analyses established the thermal stabilities of these compounds. The enthalpies of combustion of representative salts were determined using a constant volume bomb calorimetry. The data shows that these salts possess relatively high heats of combustion (ΔU_c, ca. 35 kJ·g^{-1}), and have the potential to serve as green high-energy materials.

1. Introduction

Over the past decades substantial interest has developed in insensitive munitions (IM) – high energy compounds which are relatively stable to unplanned stimuli such as heat, shock, fragment or bullet impact, or electromagnetic pulse (EMP) [1]. Ideally, the IM should be an environmentally friendly or "green" explosives as well, releasing neither smoke nor toxic gases when they detonate. Other properties desired are high crystal density and heat of formation, with a low oxygen balance. A class of compounds which would seem to answer all these criteria, are those which are rich in nitrogen and/or boron and produce primarily N_2 and boron oxides on oxidative decomposition. These materials are thermally stable and insensitive to electrical discharge, friction and impact [2,3]. Since these compounds contain fewer hydrogen and carbon atoms, oxygen balance is less of a problem.

Turning first to polynitrogen compounds, many are known to be thermallly stable energetic systems. Examples of stable nitrogen rich compounds are pyrazoles (**1**), imidazoles (**2**), 1,2,3- and 1,2,4-triazoles (**3a** and **3b**, respectively) and tetrazoles (**4**), all aromatic five-membered ringed compounds containing two, three and four nitrogen atoms respectively (see Scheme 1) [2]. Among the six-membered aromatic systems are the 1,2,3,4 and isomeric 1,2,4,5,-tetrazines (**5a** and **5b**, respectively) with four nitrogens [4].

These heterocyclic systems have been prepared with nitro, azido, nitrate and ester substituents to raise the thermal energy of these molecules [2,5]. In addition, if there is an amino group α to these groups, the thermal energy increases, due to intermolecular hydrogen bonding [5].

Regarding column IIIA elements boron and aluminium, they release large amounts of energy upon combustion, because of the

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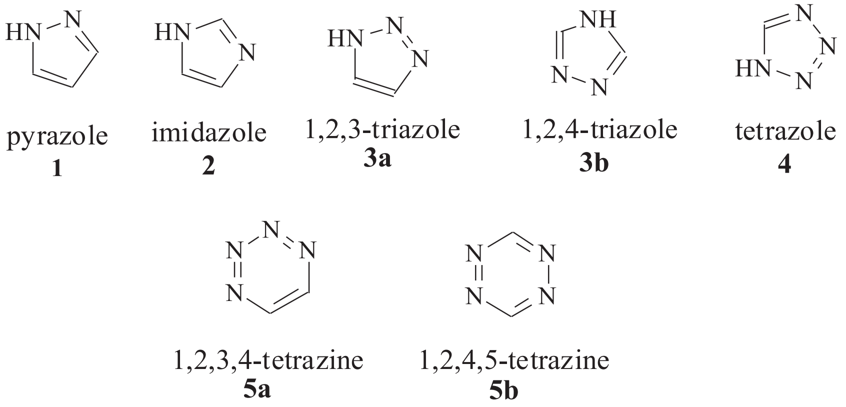
https://doi.org/10.1016/j.poly.2018.09.055

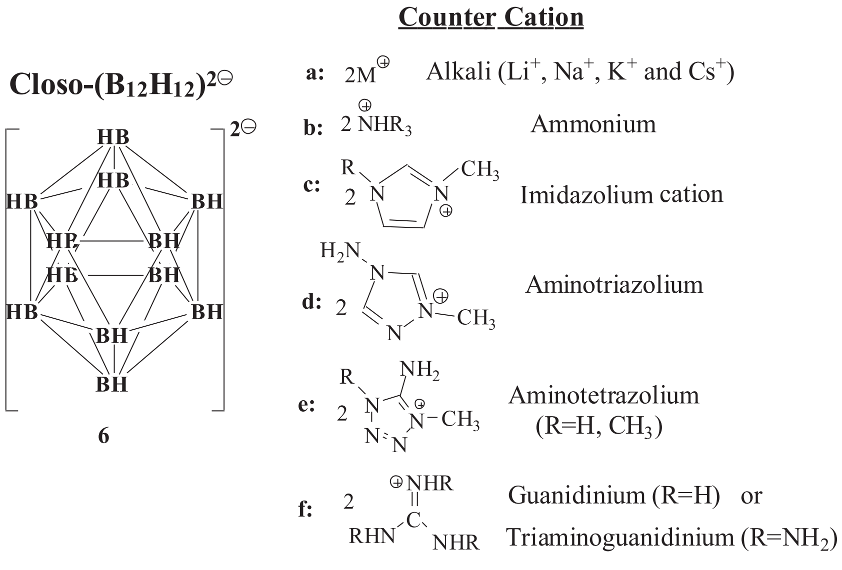


Scheme 1. Assorted polynitrogen heterocyclic aromatics.

stability of their oxidation products B_2O_3 or Al_2O_3. As a results, these elements are often added to various formulations of high-energy materials (HEM) in order to enhance their energy output [2,3,5]. Alkylammonium dodecahydroborate salts have been known since 1963 [6], and are starting materials for various metal dodecahydroborate salts [7–9]. The latter can be converted to organic dodecahydroborates by a metathesis (or cation exchange) reaction [10–13]. Lower hydroborate anions, such as closo-($B_{10}H_{10}$($^{2-}$ [14], closo-(B_6H_6($^{2-}$ [7] or $B_3H_3^-$ [15] have also been investigated,[16] but are less stable to oxidation and hydrolysis. ^{11}B NMR spectra of various hydroborate compounds have also been reported [17].

Boron salts containing a closo-($B_{12}H_{12}$($^{2-}$ system (**6** in Scheme 2) are among the most stable boron compounds. This dianionic system is a symmetrical icosahedron that contains clusters of 12 boron atoms. Each boron atom within the dodecahedryl closo system **6** is surrounded by four other delocalized boron valence electrons, which creates a δ-bonded framework on the cluster surface. The number of electrons involved in the cluster is $4n + 2$, where $n = 6$, similar to that of an aromatic system. The double negative charge in closo **6** is dispersed equally over the surface [18]. Common counter ions for **6** are alkali metal [Li^+, Na^+, K^+, and Cs^+], ammonium [NEt_3H^+ and NBu_4^+], trityl [CPh_3^+] and nitosonium [NO^+] cations [3]. The physical and chemical properties of inorganic and alkylammonium closo-($B_{12}H_{12}$($^{2-}$ compounds have been investigated [9,14]. Organic salts combining closo($B_{12}H_{12}$)$^{2-}$ anions to imidazolium, triazolium or tetrazolium cations [13] (Scheme 2) are expected to be very stable, because the heterocyclic cations maintain an aromatic structure.

Our goal in this project was to synthesize novel polyboron salts containing polynitrogen organic cations. Bis(imidazolium) and bis(triazolium)dodecahydroborate salts (**6c** and **6d**, respectively) are well-known in the literature [10–12]. We, therefore, focused our efforts on the preparation of aminotetrazolium and aminoguanidinium analogs **6e** and **6f**. The latter are good candidates for green energetic materials because of the high percentage of nitrogen [19,20]. Tetrazole rings have also been shown to be applicable in a variety of high energy salts, with the tetrazole ring serving as either part of the nitrogen rich cation, or the anion or both [21]. Aminoguanidines [22] and tetrazoles [23] also have a well-documented role in high energy compounds. Indeed, several papers have even appeared describing the synthesis of aminoguanidinium [24,25,26] and aminotetrazolium [11,27] dodecahydroborate salts. However, the procedures are not convenient and the identity of the prepared compounds was for the most part determined only by IR spectroscopy and elemental analysis. Below we describe general and relatively simple procedures for the synthesis of the desired closo($B_{12}H_{12}$)$^{2-}$ salts and report their complete spectral properties.



Scheme 2. Various dodecahydroborate salts.

2. Results and discussion

2.1. General synthetic strategies for the preparation of organic dodecahydroborate salts

Based on previous efforts [10–12], we have developed two general and convenient synthetic pathways for the preparation the dodecahydroborate organic salts, which depend on the aqueous solubility of the desired product salt. Water insoluble dodecahydroborate salts can be synthesized from the potassium or sodium salts of dodecahydroborate (**7** and **8**, respectively) by a simple metathesis (ion exchange) reaction with the corresponding chloride of the desired organic cation (Scheme 3, **Path 1**). The organic closo$(B_{12}H_{12})^{2-}$ salt precipitates and the water soluble starting materials and resulting inorganic KCl or NaCl are washed away.

Water soluble salts can be prepared via two consecutive metathesis reactions (Scheme 3, **Path 2**): in the first, the organic cation chloride is converted with silver sulfate to the corresponding water soluble organic sulfate salt and insoluble silver chloride; following filtration, the cation sulfate is reacted with barium dodecahydroborate (**9**), yielding the water soluble organic closo $(B_{12}H_{12})^{2-}$ salt and the insoluble $BaSO_4$. The product salt is conveniently isolated by water evaporation and purified by recrystallization, if necessary.

Turning now to the inorganic sodium closo$(B_{12}H_{12})^{2-}$ salt ($Na_2B_{12}H_{12}$, **8**) starting material, synthetic procedures for its preparation have been known [7,15,28,29,30] for close to 50 years. They were fraught, however, with two major drawbacks. Firstly, the starting materials used, B_2H_6 and B_4H_{10}, are toxic and costly; secondly, product isolation is often a daunting task. We did, however, succeed in preparing **8** according to the more recent and convenient procedure of Geis et al. [8], outlined in Eqs. (1)–(5).

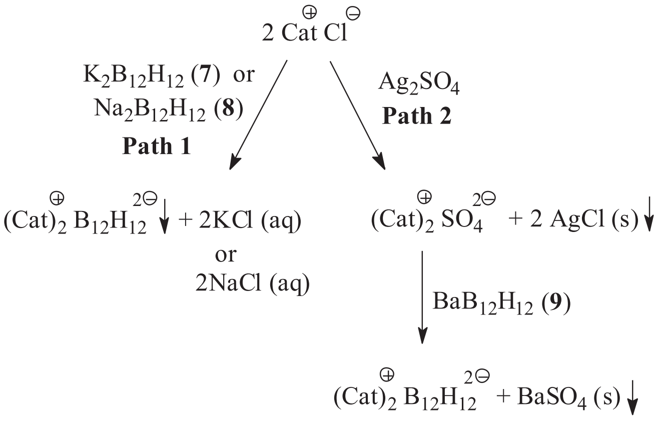
$$3NaBH_4 + I_2 \frac{\text{diglyme}}{100^\circ C, 48h} NaB_3H_8 + 2NaI + 2H_2\uparrow \tag{1}$$

$$5NaB_3H_8 + \frac{\text{diglyme}}{170^\circ C,\ 2\,hrs} + Na_2B_{12}H_{12} + 3NaBH_4 8H_2\uparrow \tag{2}$$

$$NaBH_4 + HCl + 3H_2O \rightarrow B(OH)_3 + NaCl + 4H_2\uparrow \tag{3}$$

$$Na_2B_{12}H_{12} + 2NEt_3{}^{\bullet}HCl \longrightarrow (\overset{\oplus}{H}NEt_3)_2\ B_{12}H_{12}{}^{2\ominus}\downarrow + 2NaCl \tag{4}$$

$$(\overset{\oplus}{H}NEt_3)_2B_{12}H_{12}{}^{2\ominus} + 2NaOH \xrightarrow{H_2O} \underset{\mathbf{8}}{Na_2B_{12}H_{12}} + 2NEt_3 + 2H_2O \tag{5}$$



Scheme 3. General synthesis of closo$(B_{12}H_{12})$ salts.

When we compared the chemical reactivity of the sodium salt **8** with the commercially available (Strem Chemicals) potassium salt **7**, we found no substantial difference in the yield of the resulting organic closo$(B_{12}H_{12})^{2-}$ salts. Commercial $K_2B_{12}H_{12}$ (**7**) does not contain complexed water and is relatively non-hygroscopic. By contrast, $Na_2B_{12}H_{12}$ (**8**) crystallizes from water as a solid leaf-shaped brilliant white crystal. According to elemental analysis via inductively coupled plasma (ICP) and NMR, **8** is a pentahydrate, with a molecular formula of $Na_2B_{12}H_{12}{\cdot}5H_2O$.

The barium salt $BaB_{12}H_{12}$ (**9**), used above in Path B of Scheme 3, was synthesized in a fashion analogous to the Geis procedure [8], by refluxing a dilute aqueous solution of bis(triethylammonium)-dodecahydroborate (**10**) and barium hydroxide for two hours, as outlined in Eq. (6). High dilution and heat are required for this metathesis because of the relative insolubility of the barium hydroxide. In earlier reports [31,32] the barium salt (**9**) was prepared from the ammonium salt (**10**) in two steps, by converting it to the acid $(H_2O)_2B_{12}H_{12}$ and reacting with $BaCO_3$.

$$\underset{\mathbf{10}}{(\overset{\oplus}{H}NEt_3)_2B_{12}H_{12}{}^{2\ominus}} + Ba(OH)_2 \xrightarrow[\text{reflux, 2h}]{H_2O} \underset{\mathbf{9}}{BaB_{12}H_{12}} + 2NEt_3 + 2H_2O \tag{6}$$

3. Bis(guanidinium)dodecahydroborates 12a–e

3.1. Preparation

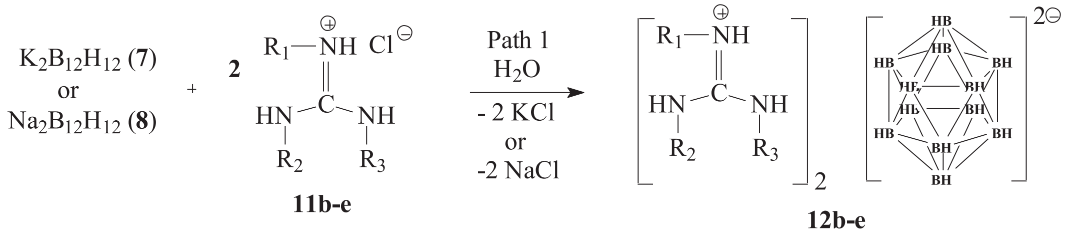
The starting materials for various derivatives of the guanidinium ions were the corresponding chlorides **11**. Guanidinium-, aminoguanidinium- and diaminoguanidinium chloride (**11a, b** and **c,** respectively) are commercially available. Triaminoguanidinium chloride **11d** was prepared according to the procedure of Coburn et al. [33], while guanylurea hydrochloride (or guanyluronium chloride) **11e** was prepared according to the approach of Klapotke and coworkers [34]. Since the corresponding bis (guanidinium) closo$(B_{12}H_{12})$ salts (**12b-e**) are water insoluble, they can be prepared directly by a single metathesis reaction (as outlined in Scheme 3, path 1). Thus chlorides **11b-e** reacted with dipotassium or disodium dodecaborohydrates (**7** or **8**, respectively), yielding the desired bis(guanidinium) closo$(B_{12}H_{12})$ salts (**12b-e**) in 70–80% yield (Scheme 4).

The procedure of Path 1 failed for analog **12a**, because of the good aqueous solubility of this closo salt. For that reason, we used the double metathesis approach (**Path 2** in Scheme 3). As shown in Scheme 5, the preparation of **12a** involves two ion exchange reactions. In the first step the halogen ion is replaced by sulfate ion, using Ag_2SO_4. Following filtration of the AgCl, $BaB_{12}H_{12}$ was added, the resulting $BaSO_4$ precipitate was filtered off, and the water evaporated to give **12a**. Organic closo salts **12a-e** were characterized by NMR, MS and ICP spectroscopy, as will be described later.

3.2. Characterization

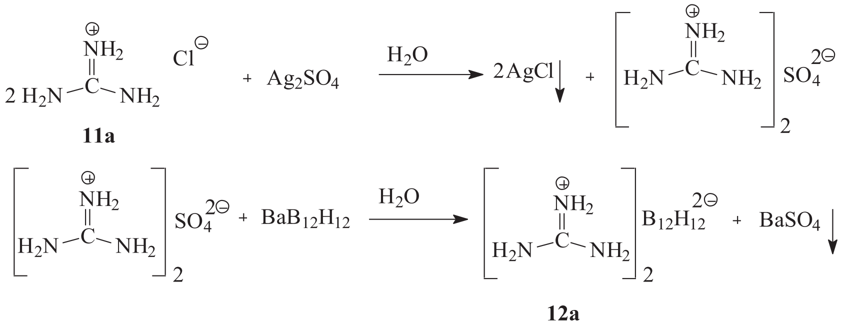
Bis(guanidinium)) closo salts **12a–e** (Schemes 4 and 5) were characterized by ^1H, ^{13}C and ^{11}B NMR, MS and ICP spectroscopy. The literature records that the counter anion has little if any affect on the ^1H or ^{13}C NMR chemical shifts of the cation within an organic salt [20,35]. Indeed, the spectra of the various cations in **12** are almost identical to the corresponding guanidinium hydrochloride starting materials **11**.

The ^1H NMR chemical shift of the $(B_{12}H_{12})^{2-}$ anion is also identical in its various salts [10–12]. Thus, there is a broad high field (0.7–1 ppm) multiplet, due to coupling of the H-B groups, which includes the ^{11}B and ^{12}B isotopes of boron (^{11}B – 80.42% and ^{10}B



b: R_1=R_2 =H, R_3=NH_2; c: R_1=H, R_2=R_3=NH_2 **d:** R_1=R_2=R_3=NH_2 **e:** R_1=R_2 =H, R_3=$CONH_2$

Scheme 4. Synthesis of bis(guanidinium) closo($B_{12}H_{12}$) salts (**12b-e**).



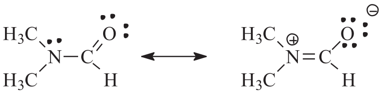
Scheme 5. Synthesis of bis(guanidinium) closo($B_{12}H_{12}$) salt **12a.**

– 19.58%) [17]. The integration ratio between the boron hydrogens to the guanidinium hydrogens confirms the stoichiometric ratio between the anion and the cation. In the ^{11}B NMR spectra, there is a doublet at −15.5 ppm, with $J_{B\text{-}H}$ = 388 Hz. To exemplify this observation, Fig. 1 shows the ^1H, ^{13}C and ^{11}B NMR spectra of **12d**. The proton ratio of internal amines:terminal amines: borohydrides is 6:12:12.

The ICP elemental analysis of boron percentage was consistent with ^1H, ^{13}C and ^{11}B NMR spectra. The ICP analysis also indicated that compound **12d** is a monohydrate. All these compounds have characteristic IR stretching appearing around 2500 cm^{-1} corresponding to stretching vibrations of the B–H bounds [10,11,24].

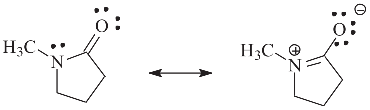
We attempted to determine the molecular structure of bis (guanidinium)dodecahydroborates analogs **12a–e** by X-ray crystallography; however, we were only able to obtain amorphous crystals from water which are unsuitable for crystal structure analysis. The literature has already indicated that most of alkylimidazolium closo($B_{12}H_{12}$) salts don't yield good [10] quality crystals. Indeed, only methyl and methyl- ethyl imidazolium derivatives have been analyzed by X-ray crystallography [12]. Aminoguanidinium closo($B_{12}H_{12}$) **12b** has been crystallized as an (aminoguanidine)copper(II):complex closo($B_{12}H_{12}$) [25]. Although bis (triaminoguanidinium)dodecahydroborate **12d** has been previously prepared [26], no X-ray crystal structure has been reported.

After some trial and error, we succeeded in obtaining good quality crystals when recrystallizing the amorphous monohydrate **12d** from DMF (dimethylfomamide). Unfortunately, the crystals obtained were far from simple and incorporated solvent. Thus, when pure DMF was used, the crystal analysis (Fig. 2) showed stoichiometric unit cell with five elements: a dodecahydroborate dianion complexed with two DMF molecules and two triaminoguanidinium cations; water is absent from the crystal. Fig. 3 is a fuller picture of the cell structure and gives us a better understanding of the complex situation. From the latter we see that the charge separated DMF molecules function to bridge between the dodecahydroborate dianion and the two guanidinium cations. In particular, the positive nitrogen end of the DMF molecules helps solvate the dianion, while the negative DMF carbonyl oxygen solvates the guanidinium cations (Eq. (7)).



(7)

When, the crystallization solvent was DMF containing a very small amount of NMP (N-methyl-2-pyrrolidone) as antisolvent, the stoichiometric unit cell (Fig. 4) contained seven elements: the dodecahydroborate dianion, two triaminoguanidinium cations, and two NMP molecules each complexed with a water molecule. Fig. 5 is a fuller picture of the cell structure, from which we see that the NMP molecules bridge between the dodecahydroborate dianion and the two guanidinium cations. In particular, the positive end of the included NMP molecules helps stabilize and solvate the dianion, while the negative NMP carbonyl oxygen does the same for the guanidinium cations (Eq. (8)). What is fascinating is that from Fig. 5 we see that each water molecules lies in between the NMP carbonyls and the guanidinium moiety. Presumably, the water proton hydrogen bonds with the pyrrolidone carbonyl oxygen, while the relatively negative oxygen end of the water interacts with the guanidinium moiety.



(8)

This incorporation of solvent into the crystal structure is characteristic of dodecahydroborate salts. For example, in the case of metal dodecahydroborate [31] crystallized from water, the salts form polyhydrates – often including as many as 15 water molecules. Similarly, tetramethyl ammonium closo($B_{12}H_{12}$) derivatives crystalize as CH_3CN complexes [30].

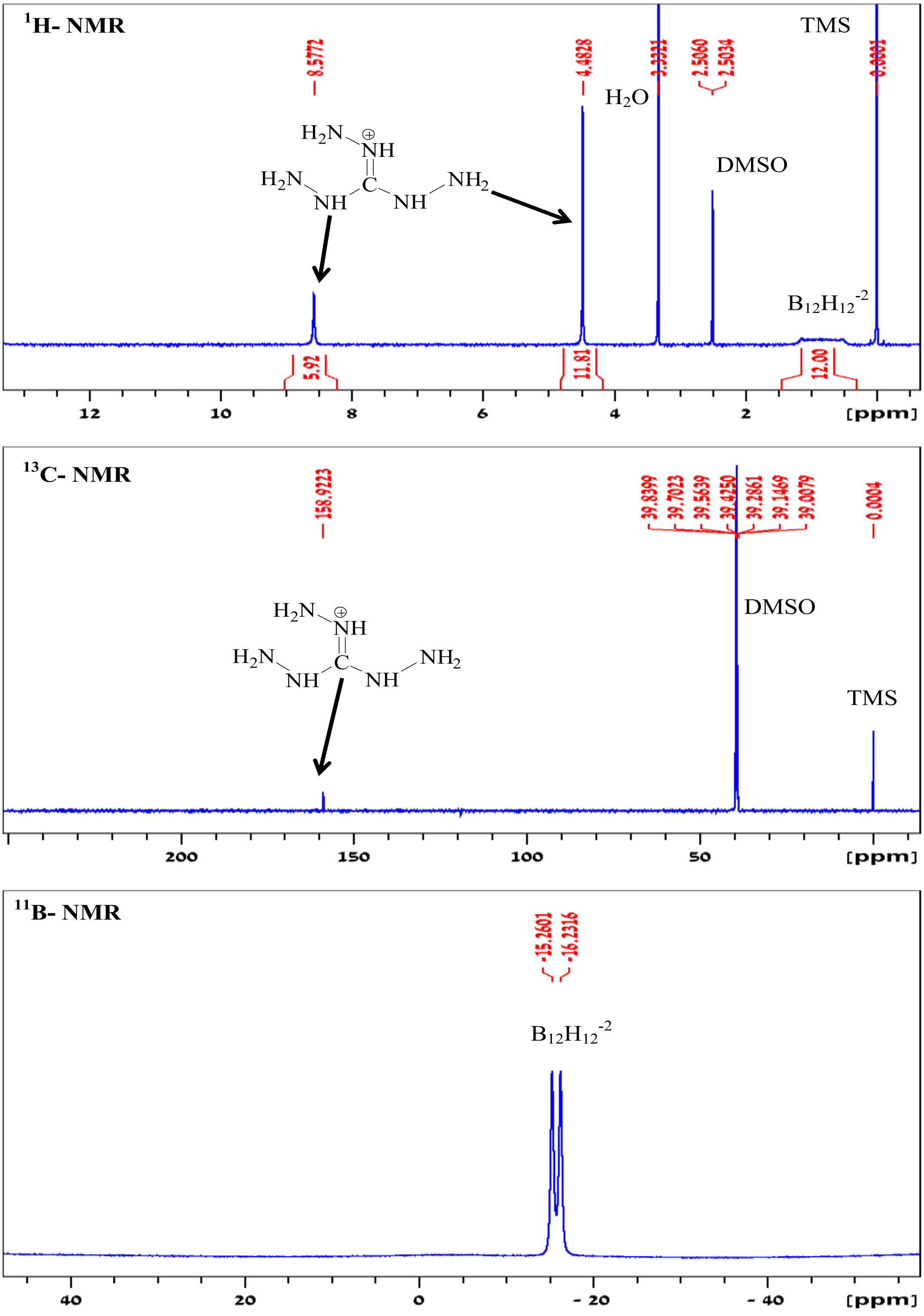
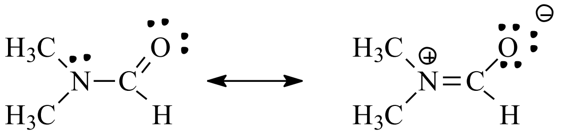


Fig. 1. ^{1}H, ^{13}C and ^{11}B NMR spectra of bis(triaminoguanidinium)dodecahydroborate **12d**.

3.3. Thermal studies

Thermogravimetric analysis (TGA) of bis(guanidinium) closo ($B_{12}H_{12}$) salts **12a–e** were carried out under N_2. The results are shown in Fig. 6.

Fig. 6 indicates that increasing amination of the guanidinium cation decreases the stability of the salt. Thus, bis(di- and triaminoguanidinium)dodecahydroborate salts **12c** and **12d** decompose at ca. 260 °C, while the corresponding unsubstituted and monoamino analogs **12a** and **12b** and guanylurea analog **12e** are somewhat more stable up to about 350 °C, presumably due to the increased number and strength of the hydrogen bonds (see Table 3). This stability decrease with increasing amination seems to be well correlated to the weight percentage of the anion in the dodecahydroborate salt. Thus, in the unsubstituted guanidine analog **12a,** the closo$(B_{12}H_{12})^{2-}$ anion comprises 54% of the



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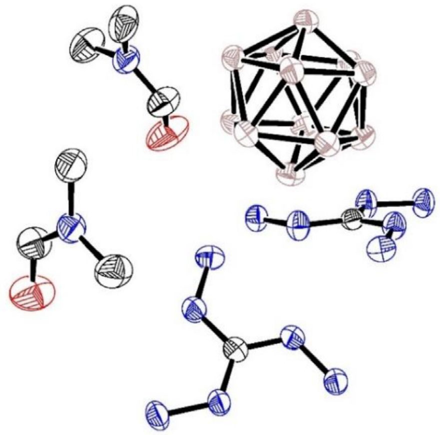


Fig. 2. Representation (hydrogens not shown) of stoichiometric unit cell of bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from pure DMF.

molecular weight, while in the triaminoguanidinium analog **12d** and in the guanylurea analog **12e** the dodecahydroborate anion weight percentage drops to 40%. Presumably, the organic part of the molecule undergoes decomposition first leaving the closo $(B_{12}H_{12})$ cluster essentially untouched. This correlation is preecedented and first observed in the TGA traces of dialkylimidazolium-dodecahydroborate salts [10]. The maximum weight loss of 40% for the compounds matches the percentage weight loss of only one guanidinium group, which consists of approximately 30% of the molecular weight in the bis(guanidinium) closo$(B_{12}H_{12})$ salts **12c–d** and in the guanylurea analog **12e** (Table 3). In the unsubstituted and monoamino guanidine dodecaborate salts **12a** and **12b**, respectively, the weight loss is only ca. 25% due to the corresponding lower molecular weight of the cation.

After the initial weight loss, the residual weight of the dodecahydroborate salts **12a–e** remains constant weight (80–60%, Table 3) – even at temperatures as high as 1000 °C. This is presumably because of the thermal stability of the closo$(B_{12}H_{12})$ anion.

The 223 °C melting point of **12d** was the lowest of the dodecahydroborate salts, while those of the other derivatives are substantially higher (>300 °C). Interestingly, this low value may correspond to the fact that the onset of decomposition for this salt occurs at approximately the same temperature as its melt (Fig. 6 and Table 3), a common phenomenon in high energy density materials.

We should note in closing this section that the aminoguanidine salts **12a–d** have been previously studied by Rao and Muralidharan in 2016 [26], and were prepared by reacting $Ag_2B_{12}H_{12}$ with the corresponding organic cation halides. These salts were reported to show a complicated TGA decomposition pattern with substantially lower melting points, compound stability and residual weight percentages (only around 30%) than recorded in the present paper. By contrast, our aminoguanidinium closo$(B_{12}H_{12})$ salts were

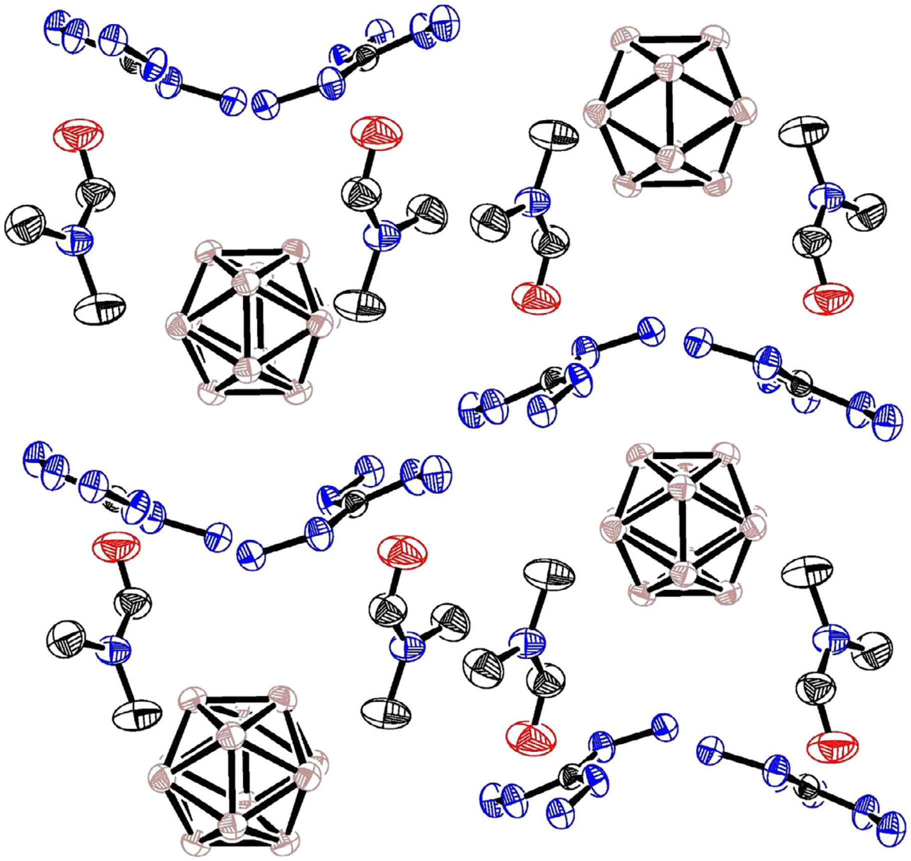
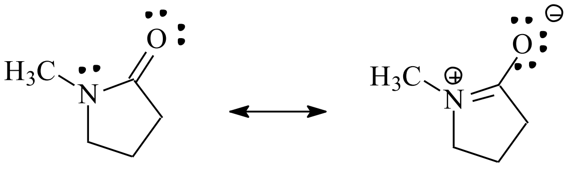


Fig. 3. Larger representation of crystal structure obtained from the bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from pure DMF (hydrogens not shown). The bridging/solvating role of the DMF can be clearly seen.



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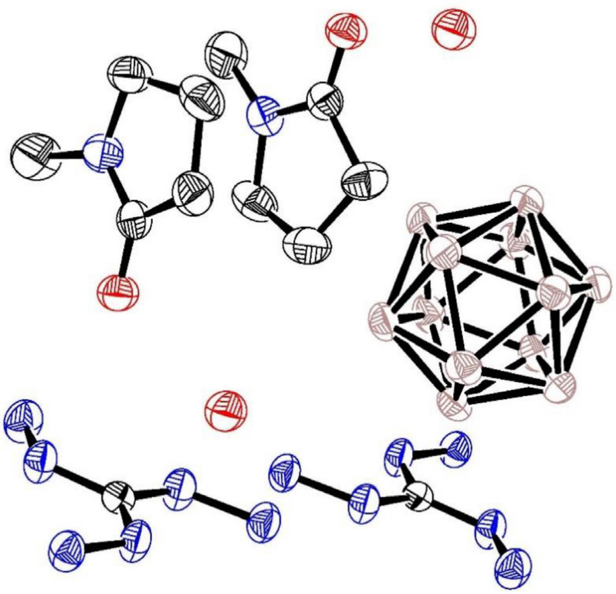


Fig. 4. Representation (hydrogens not shown) of stoichiometric unit cell of bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from DMF/NMP.

obtained via metathesis reaction with $Na_2B_{12}H_{12}$ or $K_2B_{12}H_{12}$ (**7** or **8**, respectively, for water insoluble salts) or through double metathesis reactions using $BaB_{12}H_{12}$ (**9**, for water soluble salts). They showed residual weight percentages of 60–85%, and melting points as much as 200 °C higher than those previously reported. Even the proton NMR data reported in the 2016 paper are replete with errors. For example, as shown in Fig. 1 above, the proton values for the internal amines:terminal amines: borohydrides in **12d** is: 8.59 (s, 6H), 4.48 (s, 12H), 1.60–0.30 (br m, 12H) ppm. By contrast, Rao and Muralidharan report the following values: 8.59 (s, 4H), 6.53 (s, 2H), 4.49 (s, 8H), 1.25–0.39 (br m, 12H). Because of resonance and rapid exchange, all six of the internal amine hydrogens must be identical, while the integration for the terminal hydrogens should be 12, not 8. All this clearly indicates that our aminoguanidine salts **12a–d** are by far more pure.

4. Bis(aminotetrazolium)dodecahydroborates 15 and 16

4.1. Preparation

Dodecahydroborate salts containing imidazolium or triazolium cations are known [10–12] as is the aminotetrazolium analog **15c** [11,13,27]. We synthesized derivatives of 5-aminotetrazolium cations, **15a-d** and **16a-b** (see Scheme 6), starting from 1,5-diaminotetrazole (**13**) [36,37] or the commercially available 5-aminotetrazolium monohydrate (**17**) [38,39,40], as outlined in Scheme 7.

Thus, methylation of **17** with methyl iodide under basic conditions yields monomethyl aminotetrazoles **18** and **19** [39]. The isomeric compounds were separated by crystallization of the product mixture from acetone-water solution. 1-Methyl-5-aminotetrazole (**18**) is the main product and crystallized from the solution in a 50% yield. After evaporating the mother liquid, 2-methyl-5-aminotetrazole (**19**) was recrystallized from water in a 20% yield.

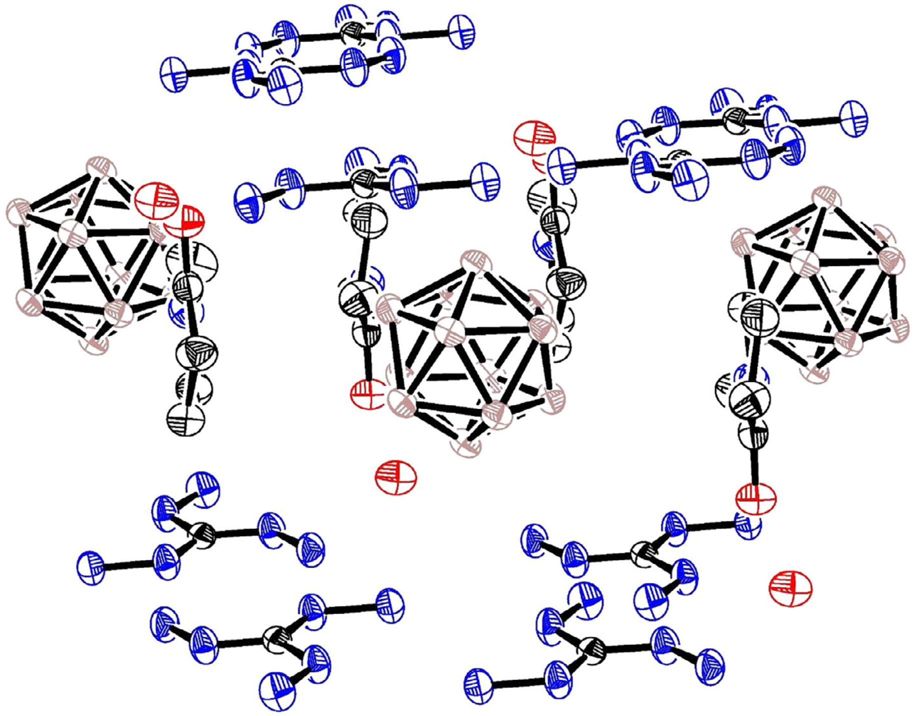


Fig. 5. Larger representation of crystal structure obtained from the bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from DMF/NMP (hydrogens not shown). The bridging/solvating role of the NMP can be clearly seen.

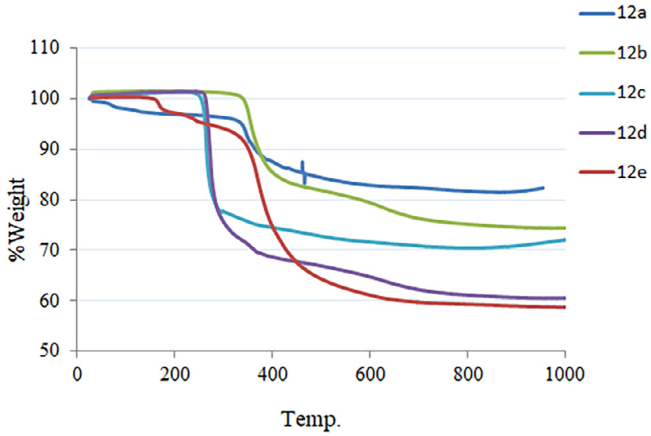


Fig. 6. TGA curves of bis(guanidinium) closo($B_{12}H_{12}$) salts **12a–e.**

Methylation of **18** and **19** with methyl iodide in refluxing acetonitrile (**Path A**) yields 1,4- and 1,3-dimethyl 5-aminotetrazolium iodide (**20a** or **21a**), respectively. Under the same "**Path A**" conditions, 1,5-diaminotetrazole **13** is converted to methyl-diaminotetrazolium iodide **14**.

Aminotetrazolium chloride (**20c**) [41] or hydrochloride salts **20b** and **21b** were prepared by refluxing aminotetrazoles **18, 19** and **17** respectively with conc. HCl (in methanol) (**Path B**). [We note that in early studies, we also prepared the corresponding sulphates [42] with conc. H_2SO_4 (in water), but found that their isolation pure was more difficult, and the overall yields leading to dodecahydroborates **15b, 15c** and **16b** were not improved].

The last step was to prepare the dodecahydroborate salts via metathesis. The unmethylated and monomethyl aminotetrazolium dodecahydroborates are water soluble due to the polar character of the cation. Hence, compounds **15b–d** and **16b** were synthesized via **Path D** from the aminotetrazolium chloride via *in situ* dual ion exchange of chloride with sulfate and the latter with dodecahydroborate (see Scheme 7). The dimethylated analogs **15a** and **16a** salts are only slightly soluble in water and could, therefore, be prepared via **Path C** (a one step ion exchange) which concludes with precipitation from water.

4.2. Characterization

Characterization of these molecules was conveniently accomplished by ^1H, ^{13}C and ^{11}B NMR, ICP and MS (see Fig. 7k). As before, the counter anion has little if any affect on the ^1H or ^{13}C NMR chemical shifts of the cation within an organic salt [20,35]. Thus the chemical shifts of the 5-aminotetrazolium dodecahydroborates are nearly identical to those of the 5-aminotetrazolium halides.

The ^1H and ^{11}B NMR chemical shift of the $(B_{12}H_{12})^{2-}$ anion is also identical in its various salts [10–12]. The ratio between the boron's hydrogens to the aminotetrazolate's methyl hydrogens confirms the stoichiometric ratio (1:2) between the anion and the cation. ^1H, ^{13}C and ^{11}B NMR spectra of **15a** are presented in Fig. 7.

The ICP elemental analysis of boron percentage was consistent with ^1H, ^{13}C and ^{11}B NMR spectra. It also indicated that compound **15a** is a monohydrate. All these compounds have characteristic IR-stretches appearing at ca. 2500 cm^{-1} corresponding to stretching vibrations of the B-H bonds [10,11,24].

4.3. Molecular structure

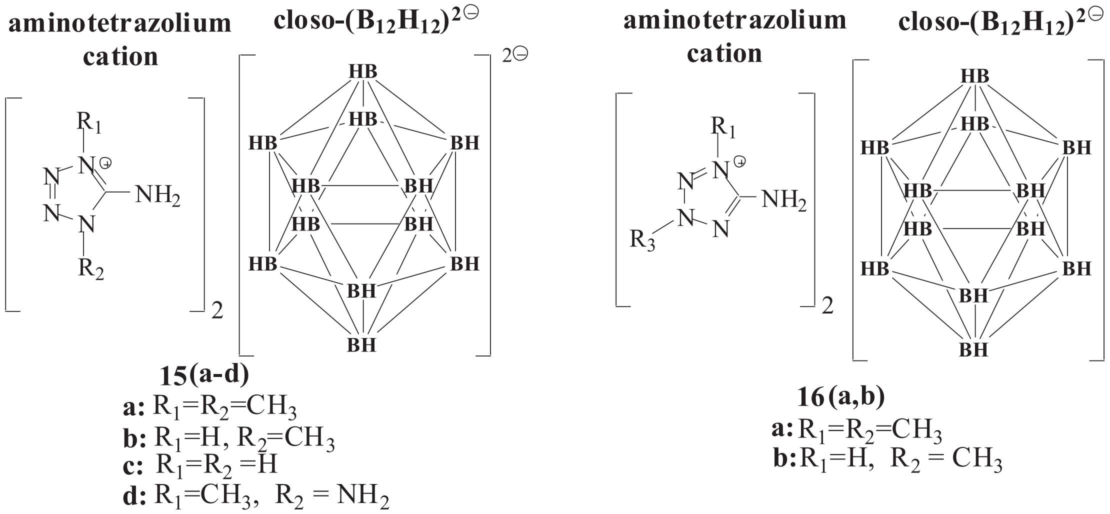
The crystal structure of the dodecahydroborate **15a** monohydrate was determined by low temperature X-ray diffraction on suitable single crystals, which were selected from a distilled water recrystallization mixture, as previously described [43]. The unit cell is shown in Fig. 7 and the corresponding data is given Table 4. As seen from Fig. 8, the unit cell of **15a** includes a water molecule which is hydrogen bonded to an amino group of one of the aminotetrazolium cations.

Crystal structures of closo($B_{12}H_{12}$) salts with metal cations have been widely investigated [30,31,32,44,45]. Some triazolium and imidazolium dodecahydroborate salts crystal structures are also known in literature [12,27], with the closo($B_{12}H_{12}$) dianion essentially unchanged in all its compounds. Similarly, the structure of the dimethylaminotetrazolium cation remains the same in various aminotetrazolate salts [38].

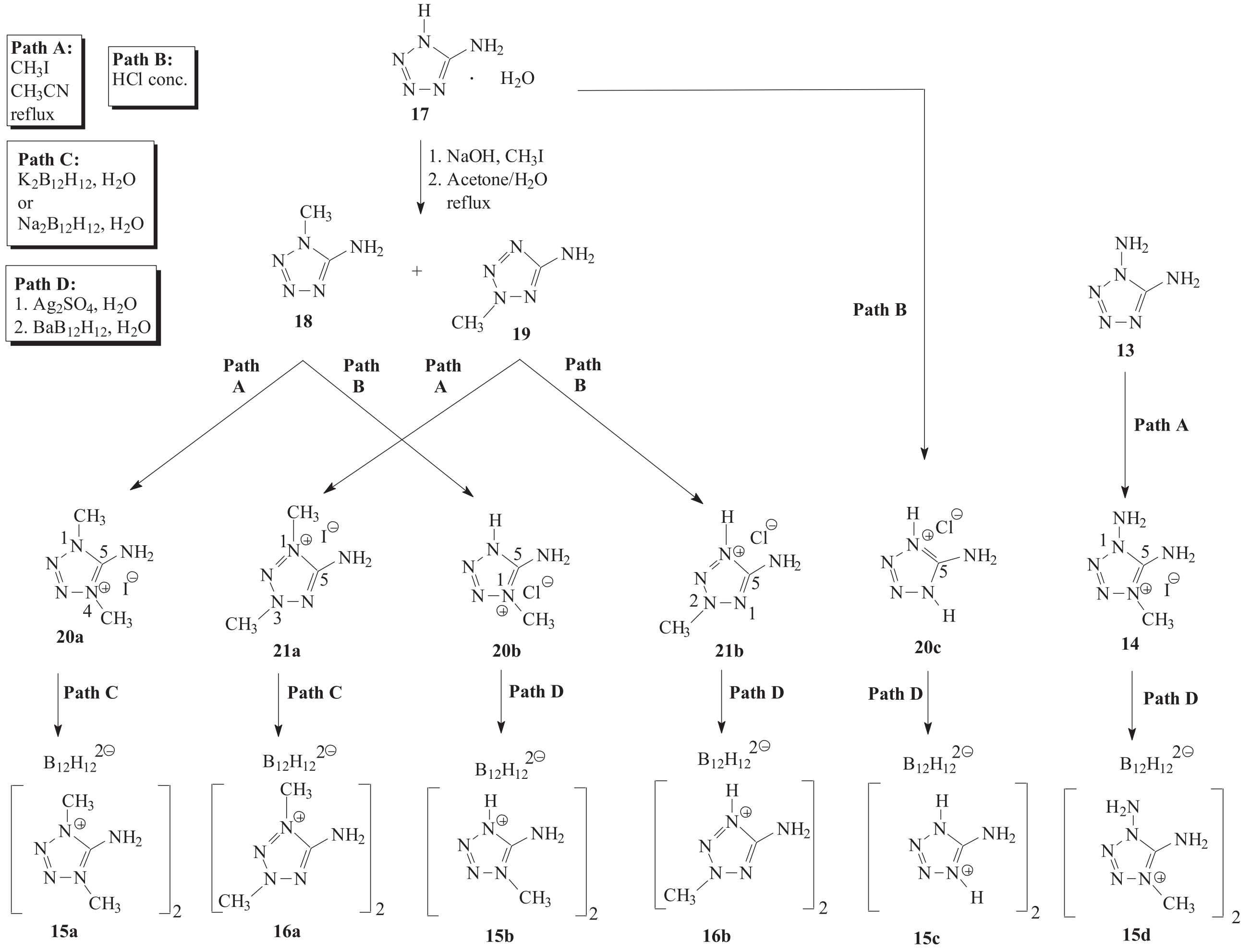
4.4. Thermal studies

The thermogravimetric analysis (TGA) under N_2 of aminotetrazolium dodecahydroborate salts **15a-d** and **16a-b** appear in Fig. 9. The data indicates that **16b** is relatively speaking the most unstable of the dodecahydroborate salts, with an onset of decomposition at 150 °C and a weight loss of 60% by 228 °C. By contrast, the onset of decomposition of the other closo salts is ca. 300 °C.

Fig. 9 indicates that **di**methyl substituted aminotetrazolium dodecahydroborate salts **15a** and **16a** undergo gradual decomposition at ca. 300 °C, losing 25–30% of weight (Table 3). The TGA



Scheme 6. Structure of various closo($B_{12}H_{12}$) tetrazolium salts **15a–d** and **16a–b.**



Scheme 7. Synthesis of various tetrazolium salts **15a–c** and **16a–b.**

decomposition curve of the **mono**methylaminotetrazolium dodecahydroborate **15b** is similar. These three compounds each have at least one methyl group substituted α to the amine moiety which seems to render it stability. The **un**methylated aminotetrazole salt **15c** is still less stable, losing 40% of its weight gradually between 100 and 300 °C. This is followed by the β-substituted monomethyl **16b**, which begins decomposition at 150 °C, losing 50% of its weight by 200 °C. The diamino analog **15d** is the most unstable, decomposing precipitously at 200 °C losing 90% of its weight – and may prove promising for propellant use.

This stability decrease seems to be well correlated with the weight percentage of the dodecahydroborate anion in each of the salts. Presumably, the aminotetrazolium organic portion of the molecule breaks down first releasing the energy needed to decompose the closo($B_{12}H_{12}$) cluster. A similar phenomenon has been previously observed for the TGA measurements of dialkylimidazolium dodecahydroborate salts.[10] In our aminotetrazolium closo($B_{12}H_{12}$) salts **15a–d** and **16a–b**, the dodecahydroborate anion weight percentage is ca. 40% in each case (see Table 5). Thus, the difference in decomposition temperatures can be attributed to the relative thermal stability of the aminotetrazolium cations (see Tables 1 and 2).

Interestingly, by ca 300 °C, most of the decomposition in the tetrazolium dodecaborohydrate salts **15a–c** and **16a–b** is complete, and the residue weight remains essentially constant (50–75%, Table 5) even up to very high temperatures (1000 °C). As noted above, however, bis(1,5-diamino-4-methyltetrazolium) dodecahydroborate salt **15d** loses most of its weight (90%) at its decomposition temperature of 200 °C. The profound instability of this compound would seem to stem from the cation, since a similar rapid TGA decomposition at 192 °C is reported [46] for the hydrazinetetrazolate salt of the same bis(1,5-diamino-4-methyltetrazolium) cation.

5. Combustion studies and calculated heats of formation of compounds 12d and 15a

To explore the possibility of using closo($B_{12}H_{12}$) salts as high energy fuels, we studied the energetic properties of two representative compounds: triaminoguanidinium closo($B_{12}H_{12}$) **12d** and dimethylaminotetrazolium dodecahydroborate **15a**. Both were monohydrates, though the former was amorphous, while the latter was crystalline. Since the oxidation of boron is an exothermic reaction, it is expected to increase the overall energy release from a propellant or explosive mixed with these compounds. The standard enthalpy of formation, enthalpy of combustion and heat of explosion are the essential characteristics of a high energy material. In our bomb calorimetric experiments (carried out at Hebrew University) in an oxygen atmosphere (30 bar, 20–40 mg sample), the enthalpies of combustion at constant volume (ΔH_c, kJ·mol^{-1}) were determined.

In a bomb calorimeter, chemical processes are carried out at a constant volume, i.e. $\Delta V = 0$. The first law of thermodynamics states that for isochoric (constant volume) process $\Delta U = Q_V$, where

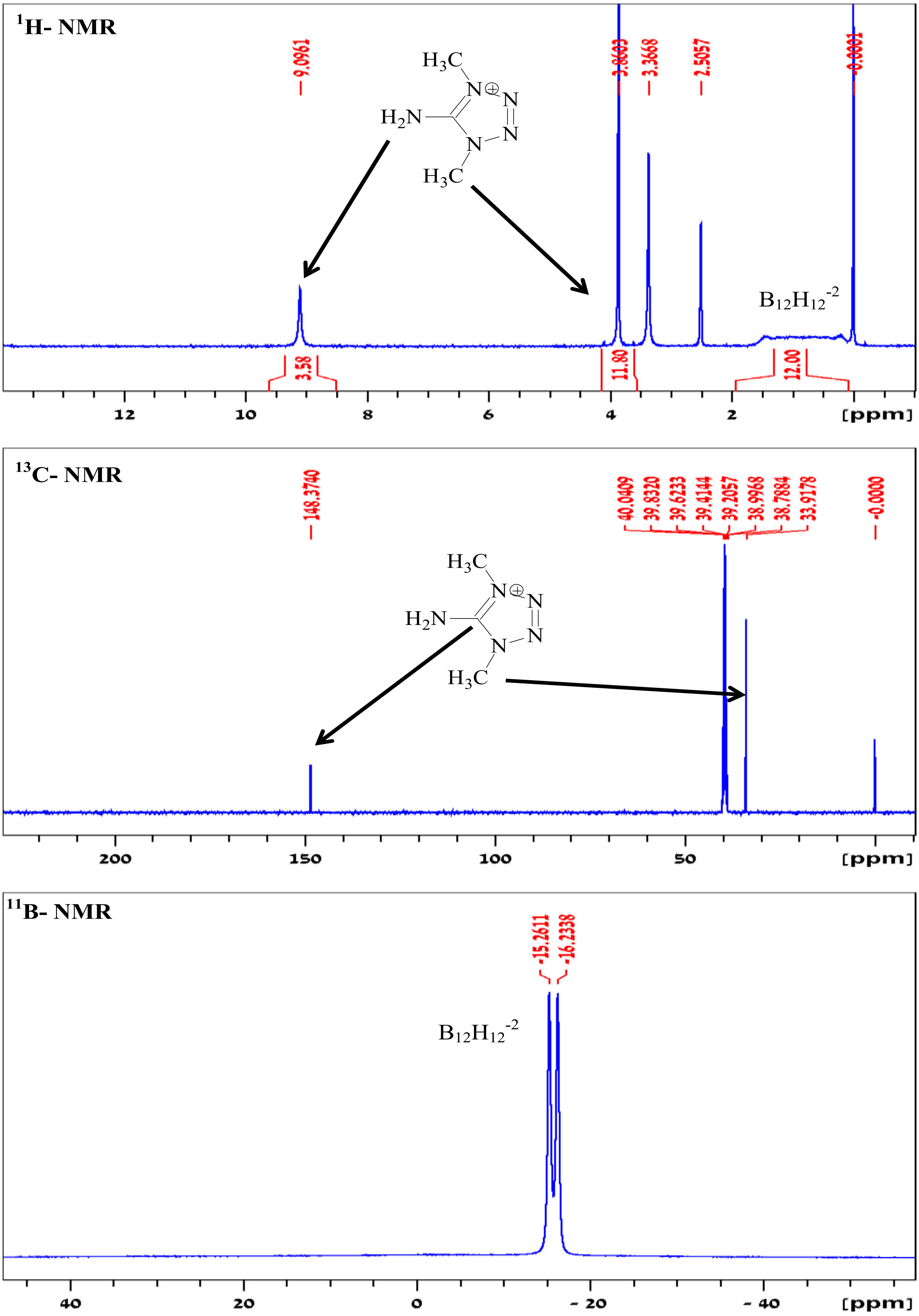


Fig. 7. ^{1}H, ^{13}C and ^{11}B NMR spectra of bis(1,4-dimethyl-5-aminotetrazolium)dodecahydroborate monohydrate**15a.**

U is the internal energy (a state function) and Q_V is the measured heat. The latter value, Q_V, is obtained in the course of calorimeter experiments and is reported as ΔU_c (kJ·mol^{-1} or kJ·g^{-1}) i.e. the change in the internal energy of the system due to the combustion process. For computational convenience, it is conventional to report the standard combustion enthalpy, i.e. $\Delta H°_C$, which is referenced to the standard state of 25 °C (298.15 K) and 1 bar (100 kPa). Recalling that $H = U + PV$, we can write directly that

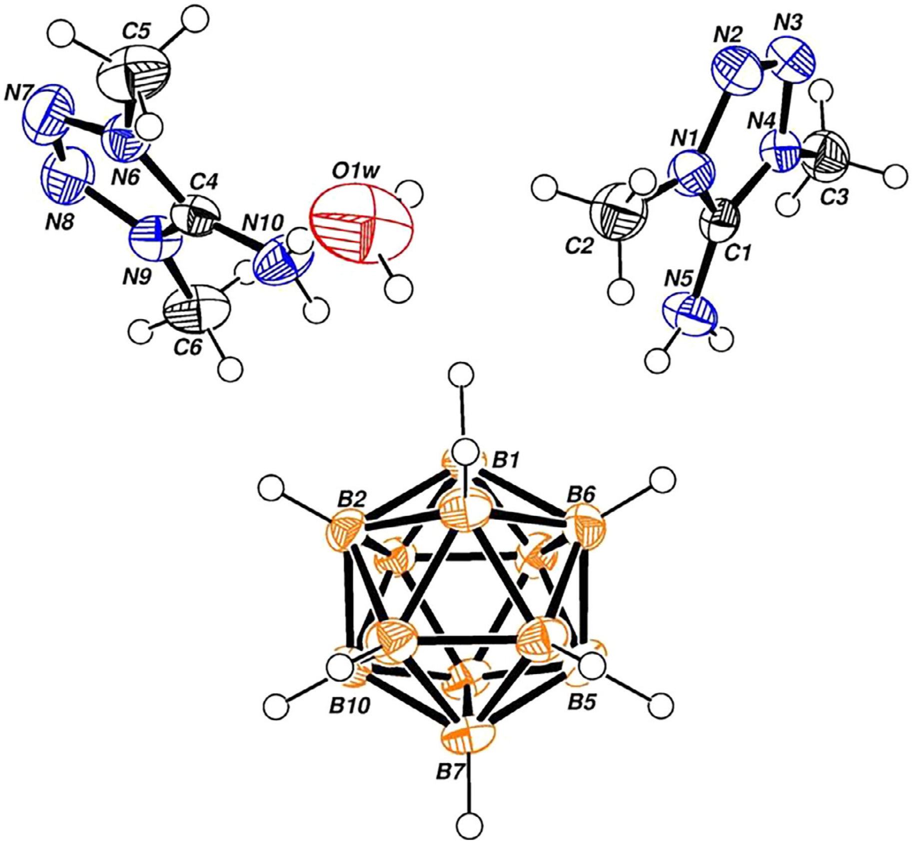


Fig. 8. Representation of stoichiometric unit cell of bis(1,4-dimethyl-5-aminotetrazolium)dodecahydroborate monohydrate **(15a)**.

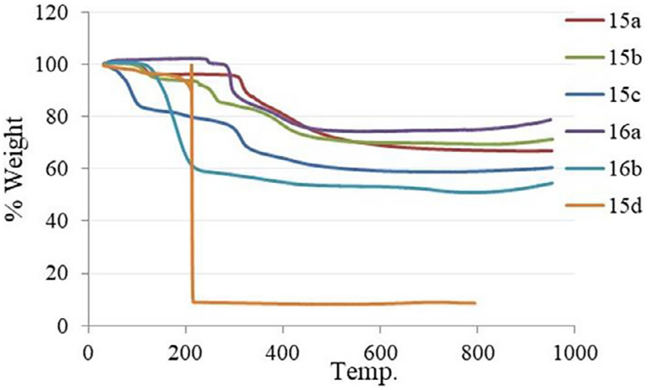


Fig. 9. TGA curves of aminotetrazolium dodecahydroborates **15a–d** and **16a–b**.

$\Delta H°_C = \Delta U°_C + (P\Delta V)°_C$. Furthermore, resorting to the Mendeleev-Clapeiron gas law, $P\Delta V = \Delta n{\cdot}RT$, we obtain $\Delta H°_C = \Delta U°_C + \Delta n_C{\cdot}RT°$. Taking into the account that the calorimetric experiments are performed at temperatures relatively close to 25 °C (in actuality, T in these experiments is ca. 22 °C), we get: $\Delta H°_C = Q_V + \Delta n_C{\cdot}RT°$.

To exemplify our calculations, let us turn now to the combustion of bis(1,4-dimethyl-5-aminotetrazolium)-closo-dodecahydroborate monohydrate (**15a**). It is important to note that the literature [10,26] generally assumes that the combustion products in the case of organoboron compounds are dehydrated completely (briefly designated "complete") yielding boric anhydride (O═B–O–B═O). This assumption would lead to Eq. (9a):

Table 1
Crystallographic data and structure refinement for bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from pure DMF.

Empirical formula	$C_8H_{44}B_{12}N_{14}O_2$	
Formula weight	498.29	
T (K)	294(1)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	$C2/c$	
Unit cell dimensions	a = 9.046(1) Å	α = 90°
	b = 17.402(2) Å	β = 100.807(2)°
	c = 17.822(2) Å	γ = 90°
V (Å^3)	2755.6(6)	
Z	4	
D_{calc} (mg/m^3)	1.201	
Absorption coefficient (mm^{-1})	0.078	
F(0 0 0)	1064	
Crystal size (mm^3)	0.36 × 0.33 × 0.33	
Theta range for data collection	2.34–28.01°	
Index ranges	$-11<=h<=11$, $-22<=k<=22$, $-23<=l<=23$	
Reflections collected	15 032	
Independent reflections	3265 [R_{int} = 0.0276]	
Completeness to theta = 28.01°	98.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9747 and 0.9724	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3265/0/225	
Goodness-of-fit on F^2	1.067	
Final R indices [I > 2sigma(I)]	R_1 = 0.0446, wR_2 = 0.1302	
R indices (all data)	R_1 = 0.0521, wR_2 = 0.1369	
Largest difference in peak and hole (e Å^{-3})	0.185 and −0.285	

Table 2
Crystallographic data and structure refinement for bis(triaminoguanidinium)dodecahydroborate (**12d**) recrystallized from DMF/NMP.

Empirical formula	$C_{12}H_{52}B_{12}N_{14}O_4$	
Formula weight	586.40	
T (K)	293(1)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 13.970(3) Å	$\alpha = 90°$
	b = 12.978(2) Å	$\beta = 97.633(3)°$.
	c = 17.563(3) Å	$\gamma = 90°$
V (Å^3)	3156.0(10)	
Z	4	
D_{calc} (Mg/m^3)	1.234	
Absorption coefficient (mm^{-1})	0.083	
F(0 0 0)	1256	
Crystal size (mm^3)	0.42 × 0.21 × 0.18	
Theta range for data collection	2.15–27.00°	
Index ranges	−17<=h<=17, −16<=k<=16, −22<=l<=22	
Reflections collected	16 612	
Independent reflections	3423 [R_{int} = 0.0328]	
Completeness to theta = 27.00°	99.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9852 and 0.9660	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3423/0/294	
Goodness-of-fit on F^2	1.076	
Final *R* indices [*I* > 2sigma(*I*)]	R_1 = 0.0471, wR_2 = 0.1254	
R indices (all data)	R_1 = 0.0564, wR_2 = 0.1312	
Largest difference in peak and hole (e Å^{-3})	0.290 and −0.252	

$$(C_6N_{10}H_{16})(B_{12}H_{12})\cdot H_2O_{(Solid)} + 22O_{2\ (Gas)} \rightarrow 6CO_{2\ (Gas)} + 5N_{2\ (Gas)} + 6B_2O_{3\ (Solid)} + 15H_2O_{(Liq)} \tag{9a}$$

From the calorimetry experiment we obtain:
$Q_V = \Delta U°_C = -35.97$ kJ/g or -13960.6 kJ/mole
$\Delta n_C = 6 + 5 - 22 = -11$
$\Delta n_C \cdot RT° = (-11) \times (8.314) \times (298.15) = -27.27$ kJ·mol^{-1}
$\Delta H°_C = -13960.6 - 27.27 = -13988$ kJ·mol^{-1}
The standard enthalpy of formation is defined as (Eq. (10)):

$$\Delta H^{\circ}_{C} = \sum n_i \times \Delta H^{\circ}_{f}(\text{product}_i) - n_i \times \Delta H^{\circ}_{f}(\text{reactant}_j) \tag{10}$$

which leads to the following result for the standard formation enthalpy of **15a**

$$\Delta H^{\circ}_{f}(\mathbf{15a}) = -\Delta H^{\circ}_{C}(\mathbf{15a}) + 6\Delta H^{\circ}_{f}(CO_2) + 6\Delta H^{\circ}_{f}(B_2O_3) + 15\Delta H^{\circ}_{f}(H_2O) \tag{11a}$$

For the $\Delta H°_f$ values, we use those given on the NIST website [47],
$\Delta H°_f(CO_2) = -393.5$ KJ/mol; $\Delta H°_f(B_2O_3) = -1273.5$ KJ/mol; $\Delta H°_f(H_2O) = -285.8$ kJ/mol
Thus: **$\Delta H_f°(\mathbf{15a})_{complete} = -301$ kJ·mol^{-1} (or -71.9 Kcal mol^{-1})**

Surprisingly, however, in the case of closo($B_{12}H_{12}$) salts **15a** and **12d**, a non-explosive oxidation of the substances is observed leading to the formation of nano-crystalline **orthoboric acid** [$B(OH)_3$ or H_3BO_3] **as the main crystalline product** presumably accompanied by some oxoborinic acid (HBO_2). We note that in both $B(OH)_3$ and O═B–O–B═O, boron has the some oxidation number (+3); however, the former is incompletely dehydrated (briefly designated "incomplete." Again, carbon dioxide and molecular nitrogen are the main gaseous products – but no water is produced. The formation of crystalline orthoboric acid was confirmed by powder XRD and Raman spectroscopy on the residual solids collected from the bomb after each experiment. This surprising result requires a revision of our combustion reaction to Eq. (9b):

$$(C_6N_{10}H_{16})(B_{12}H_{12})H_2O_{(Solid)} + 22O_{2(Gas)} \rightarrow 6CO_{2(Gas)} + 5N_{2(Gas)} + 9H_3BO_{3(Solid)} + 3HBO_{2(Solid)} \tag{9b}$$

From the calorimetry experiment we obtain:
$Q_V = \Delta U°C = -35.97$ kJ/g or -13960.6 kJ/mole
$\Delta n_C = 6 + 5 - 22 = -11$
$\Delta n_C \cdot RT° = (-11) \times (8.314) \times (298.15) = -27.27$ kJ·mol^{-1}
$\Delta H°C = -13960.6 - 27.27 = -13988$ kJ·mol^{-1}
The standard enthalpy of formation is defined as:

$$\Delta H^{\circ}C = \sum n_i \times \Delta H^{\circ}_{f}(\text{product}_i) - n_i \times \Delta H^{\circ}_{f}(\text{reactant}_j) \tag{10}$$

which leads to the following result for the standard formation enthalpy of **15a**

$$\Delta H^{\circ}_{f}(\mathbf{15a}) = -\Delta H^{\circ}_{C}(\mathbf{15a}) + 6\Delta H^{\circ}_{f}(CO_2) + 9\Delta H^{\circ}_{f}(H_3BO_3) + 3\Delta H^{\circ}_{f}(HBO_2) \tag{11b}$$

For the $\Delta H°_f$ values, we again use those given on the NIST website [47],
$\Delta H°_f(CO_2) = -393.5$ KJ/mol; $\Delta H°_f(H_3BO_3) = -1094.8$ KJ/mol; $\Delta H°_f(HBO_2) = -802.8$
Thus: **$\Delta H_f°(\mathbf{15a})_{incomplete} = -635$ kJ·mol^{-1} (or -151.8 Kcal mol^{-1}).**

We note that at 1 bar of oxygen, which is only slightly above the stoichiometric ratio of O_2 to the organic material, the oxidation process does not proceed completely to orthoboric acid [$B(OH)_3$], and a black solid (unidentified at this point) remains. This incomplete oxidation results in reduced values of the heat of combustion. Nevertheless, the heat of combustion values of the closo($B_{12}H_{12}$) salts **12d** and **15a** at 1 bar of O_2 are close to those observed at 30 bar of O_2 – leading to the conclusion that these substances are of interest for propellant applications. A non-explosive, self-sustained exothermic chemical reaction is evident. Overall, the dodecahydroborate salts **12d** and **15a** are easily ignitable and release good amounts of energy per gram (see below).

The corrected combustion equations for compounds **12d** and **15a** monohydrates are given in Eqs. (12) and (9b) respectively.

$$(C_2N_{12}H_{18})(B_{12}H_{12})H_2O_{(Solid)} + 18.5O_{2\ (Gas)} \rightarrow 2CO_{2\ (Gas)} + 6N_{2\ (Gas)} + 10H_3BO_{3\ (Solid)} + 2HBO_{2\ (Solid)} \tag{12}$$

$$(C_6N_{10}H_{16})(B_{12}H_{12})H_2O_{(Solid)} + 22O_{2\ (Gas)} \rightarrow 6CO_{2\ (Gas)} + 5N_{2\ (Gas)} + 9H_3BO_{3\ (Solid)} + 3HBO_{2\ (Solid)} \tag{9b}$$

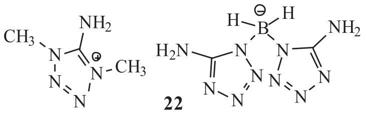
Table 3
Energetic and chemical properties of guanidinium closo($B_{12}H_{12}$) salts **12a–e**.

Compd.	T_d(°C) onset	MW Anhyd.	% Wt $B_{12}H_{12}^{2-}$	Calculated % Wt loss of one guanidinium unit	Measured % weight loss
12a	*340*	262	*54*	*23*	18
12b	340	*292*	*49*	*26*	25
12c	*260*	*322*	*44*	*28*	30
12d	*260*	*352*	*40*	*30*	38
12e	340	*348*	*41*	*30*	40

Table 4
Crystallographic data and structure refinement for bis(1,4-dimethyl-5-aminotetrazolium)dodecahydroborate monohydrate (**15a**).

Empirical formula	$C_6H_{30}B_{12}N_{10}O$	
Formula weight	388.12	
T (K)	295(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.410(2) Å	α = 80.185(3)°
	b = 10.357(2) Å	β = 80.907(3)°
	c = 13.226(3) Å	γ = 71.338(3)°
V (Å^3)	1068.8(4)	
Z	2	
D_{calc} (mg/m^3)	1.206	
Absorption coefficient (mm^{-1})	0.074	
F(0 0 0)	408	
Crystal size (mm^3)	0.30 × 0.24 × 0.18	
Theta range for data collection	2.45–28.11°	
Index ranges	$-11<=h<=11$, $-13<=k<=13$, $-17<=l<=17$	
Reflections collected	12 410	
Independent reflections	4981 [R_{int} = 0.0259]	
Completeness to theta = 28.11°	95.6%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4981/0/330	
Goodness-of-fit on F^2	1.026	
Final R indices [$I > 2\text{sigma}(I)$]	R_1 = 0.0536, wR_2 = 0.1492	
R indices (all data)	R_1 = 0.0666, wR_2 = 0.1582	
Largest difference in peak and hole (e Å^{-3})	0.217 and −0.230	

The calculated energetic data of closo($B_{12}H_{12}$) salts **12d** and **15a** is displayed in Table 6 in comparison with than a variety of representative energetic compounds pure boron, carbon, silicon, RDX, various high nitrogen containing salts prepared by Klapotke and coworkers [48], and a dihydroborate salt **22** prepared by Sharon et al [49].


22

1,4-Dimethyl-5-aminotetrazolium dihydrobis(5-aminotetrazolyl)borate

The results indicate that closo($B_{12}H_{12}$) salts **12d** and **15a** possess relatively high heats of combustion (ΔU_c, ca. 35 kJ·g^{-1}) and as seen from Table 6, these values are higher carbon, silicon, RDX and TAG [48]. Indeed, only pure boron powder has a higher heat of combustion, 58.7 kJ·g^{-1}; pure boron, however, has inefficient pyrolyzability [10].

As already noted in Section 2.3 above, triaminoguanidinium dodecahydroborate **12d** has been previously synthesized by Rao and Muralidharan [26]. These authors also studied the calorimetric parameters of their samples and report lower heat of combustion values than reported here. The differences can be attributed to three sources. Firstly, as discussed above (Section 2.3), the purity of their **12d** samples was substantially lower than ours. In addition our sample is a monohydrate while their's was reported to be anhydrous. Finally, their combustion equation assumes complete dehydration to boric anhydride (O═B–O–B═O), while we observe H_3BO_3 as the main crystalline oxidation product. Clearly, all these discrepancies will lead to conflicting results.

The oxygen balance of all these compounds is also given in Table 6. Although the oxygen balance is not encouraging, the overall thermal data shows that the closo($B_{12}H_{12}$) salts **12d** and **15a** can be useful as additives in high energy materials.

6. Conclusion

We have described the successful preparation and characterization of bis(guanidinium)dodecahydroborates **12a–e** and bis

Table 5
Thermal properties of aminotetrazolium closo($B_{12}H_{12}$) **15a–d** and **16a–b**.

Compd.	T_d(°C) onset	MW Anhyd.	% Wt $B_{12}H_{12}^{2-}$	Calculated % wt loss of one tetrazolium unit	Measured % wt loss
15a	320	370	*38*	31	33
15b	250, 350[a]	342	*42*	29	30
15c	100, 280[a]	314	*45*	27	40
15d	200	372	*38*	*31*	90
16a	280	*370*	*38*	*31*	25
16b	150	*342*	*42*	*29*	*50*

[a] Two decomposition stages.

Table 6
Thermochemical results of calorimetric measurements for closo($B_{12}H_{12}$) salts **12d** and **15a**, dihydroborate **22** [49] and other relevant compounds [48].

Substance/MW	P(O_2) in bomb, bar	Heat of Combustion, ΔU_c, kJ·g^{-1}	Enthalpy of Combustion, ΔH_c, kJ·mol^{-1}	Enthalpy of Formation, ΔH_f, kJ·mol^{-1}	Oxygen balance, %
12d/370.1	30	34.95	−12960.4	−380.2	−160.0
12d	1	28.64 (82%)			
15a/388.1	30	35.97	−13987.8	−634.8	−181.4
15a	1	34.70 (96.5%)			
22/295.1 [49]	30	18.19	−5360.0	+725.6	−100.3
Boron [48]		58.7			−222.0
Carbon [48]		32.8			−266.7
Silicon [48]		32.4			−113.9
RDX/222.1 [48]		9.53	−2105	+66.5	−21.6
TAG-DN[a]/211.2 [48]		9.65	−2027	+250	−18.9
TAG-1-Me-AtNO$_2^b$/248.25 [48]		14.00	−3465	+569	−64.46

[a] TAG-DN: Triaminoguanidinium dinitramide, $CN_6H_9^+$ $N(NO_2)_2^-$.
[b] TAG-1-Me-AtNO$_2$: Triaminoguanidinium 1-methyl-5-nitriminotetrazolate.

(aminotetrazolium)dodecahydroborates **15a–d** and **16a–b** – all green nitrogen and boron rich compounds. Our calorimetry studies on the closo($B_{12}H_{12}$) salts **12d** and **15a** indicate that they possess relatively high heats of combustion (ΔU_c, ca. 35 kJ·g^{-1}), and are, therefore, worthy of further investigation as high energy materials. We are are considering a possible role of these compounds as fire retardant additives in intumescent formulations [50].

7. Experimental

7.1. General

Nuclear magnetic resonance (NMR) spectra were recorded on a variety of Bruker Fourier transform spectrometers: Avance III-300 MHz, Avance I-400 MHz or Avance III-600 MHz. ^{1}H and ^{13}C NMR chemical shifts are expressed in δ (ppm) relative to tetramethylsilane (TMS). NMR spectra were generally run at 25 ± 1 °C and recorded while locked on the deuterium signals of the sample solvent. ^{11}B NMR spectra were recorded on Bruker DMX 400 MHz instrument relative to $BF_3{\cdot}Et_2O$ (^{11}B{^{1}H} 128.36 MHz). In the case of the known compounds, the spectral data is reported here because our data is more exact, complete or involves different - usually more convenient - solvents. **ESI-MS** was measured on a Waters (UK) Q-TOF micro MS system in positive and negative mode. **HRMS** was carried out on a 6545 Q-TOF LC/MS system (Agilent) in ESI positive and negative mode. **ICP** elemental analyses (via inductively coupled plasma) were performed on an Horiba Jovine (Ivon, France) Ultima II instrument. **Infrared spectra** were taken neat on a Nicolet iS10, Thermo Scientific USA FTIR. Only the significant peaks (medium intensity and greater) are listed. **TG-DTA analyses** was carried out under nitrogen atmosphere, with a heating rate of 20 °C/min until 1000 °C, and recorded using a Perkin–Elmer Pyris 1. **Melting points** were determined on Buchi 510 capillary melting point apparatus. **X-ray spectroscopy** was carried out on a single crystal of the sample in a Bruker Smart Apex CCD X-ray diffractometer system controlled by a Pentium-based PC using the Smart-NT V5.6 (Bruker AXS GMBH, D-76181 Karlsruhe - Germany, 2002) software package. **Heats of combustion** were determined using an isoperibol bomb calorimeter (Parr 6200). The samples were burned in an oxygen pressure of 3 MPa (30 atm.). Typically combustion values were obtained as an average of three experiments of the same sample. $Na_2B_{12}H_{12}$ was prepared as described by Gies [8], while $K_2B_{12}H_{12}$ was purchased from Strem Chemicals (Newburyport, MA). Aqueous Ag_2SO_4 solution was prepared by heating the mixture at 35 °C to dissolution and then allowing it to cool to room temperature. All other chemicals, not prepared as described below, were purchased commercially (Sigma-Aldrich, Fluka or Acros Organics) and were analytical grade. They were used as received – unless otherwise stated.

7.2. Barium dodecahydroborate·4H_2O (**9**)

A 250 mL Erlenmeyer flask fitted with a magnetic stirrer was charged with distilled water (100 mL) and bis(triethylammonium)-dodecahydroborate (**10**, 1.6 g, 4.6 mmol). The reaction flask was immersed in an oil bath at 100 °C, yielding an almost clear solution. $Ba(OH)_2{\cdot}8H_2O$ (1.45 g, 4.6 mmol) was added, the reaction was stirred at 100 °C for an hour, and then allowed to cool to room temperature overnight. A small amount of unidentified solid precipitated and was gravity filtered. The reaction solution was then divided equally into two polypropylene (less sticking) beakers (250 mL). Each beaker was immersed in an oil bath at 115 °C and the liquid was evaporated to dryness yielding a bright white solid. The product was dried in a dessicator yielding 1.15 g (3.2 mmol, 70% yield) of dodecahydroborate **9**.

^{1}H NMR (D_2O): δ 1.90–0.50 (br m, 12H) ppm. ^{11}B NMR (D_2O): δ −15.53 (d, J_{BH} = 125 Hz) ppm. FTIR: 3586, 2500, 1613, 1072, 718 cm^{-1}. HRMS (*m/z*): calcd for $[Ba^{2+} + H^-]^+$ 138.91252, obsd 138.91253; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd. 141.20547. ICP: calcd for B, 37.39%, found 38.40%; calcd for Ba, 38.81%; found: 37.30%.

7.3. Bis(triethylammonium)dodecahydroborate·4H_2O (**10**) [8]

$NaBH_4$ (10 g, 0.26 mol) was added to a 100 mL round bottom (R. B.) flask containing rapidly magnetically stirred dry diglyme (40 mL), yielding a suspension. The flask was fitted with a pressure equalizing addition funnel, whose stem reached below the reaction mixture surface. The addition funnel was charged with a solution of iodine (20 g, 0.08 mol) in diglyme (35 mL). (The solution was prepared by stirring iodine in diglyme overnight). The entire apparatus was flushed with argon and remained under an argon atmosphere during the reaction. The reaction flask was immersed in an oil bath and heated to 95–98 °C. Then the iodine was added dropwise to the flask over a 6 h period. During the addition, the gases H_2 and some B_2H_6 are formed which escape to the hood through the silicon bubbler. During the addition, the amount of insoluble $NaBH_4$ decreased and a yellow color is observed. The addition funnel was disassembled, and the R.B. flask was fitted with a reflux condenser. The entire apparatus was flushed with argon and stirred overnight at 100 °C under argon to complete the conversion to $(B_3H_8)^-$. The temperature of the oil bath was then increased to 185 °C and the reaction was refluxed overnight once more to complete the disproportionation of $(B_3H_8)^-$ to $(B_{12}H_{12})^{2-}$ and $(BH_4)^-$. At this stage, a thick white precipitate formed, and the reaction mixture was allowed to cool to room temperature. The diglyme was removed by vacuum distillation (ca 1 Torr). Most of the solvent distilled off at around 40 °C, as the oil bath temperature rose to 100 °C. The bath was finally heated to 140 °C to complete the distillation. The remaining white solid was transferred to a 250 mL Erlenmeyer flask with 60 mL of distilled water. The Erlenmeyer was immersed in a water–ice bath fitted with a magnetic stirrer, and concentrated HCl (28 mL, 0.28 mol) was added carefully to the solution as H_2 gas evolved. The acidified solution was stored in the refrigerator (+4 °C) overnight. A white solid (3–5 g, identified by ^{11}B NMR in D_2O as boric acid) precipitated and was removed by vacuum filtration. Freshly distilled triethylamine (40 mL, 0.29 mol) was carefully added to the filtrate and the cloudy solution was magnetically stirred overnight to complete the precipitation. The white solid (5 g), collected by vacuum filtration, contained large amounts of boric acid. The solid was re-suspended in 25 mL of water in an Erlenmeyer flask, fitted with a thermometer and heated briefly on a hot-plate to 60 °C. The hot suspension was quickly vacuum filtered and the solid dried in a dessicator. The bright white solid obtained (2.6 g, 7.5 mmol, 49% yield) was identified by its spectral data as dodecahydroborate **10** and appeared free of impurities.

^{1}H NMR (D_2O): δ 3.23 (q, 12H, J = 5.7 Hz), 1.30 (t, 18H, J = 5.7 Hz), 1.90–0.50 (br m, 12H) ppm. ^{11}B NMR (D_2O): δ −15.66 (d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (D_2O): δ 47.35, 8.87 ppm. FTIR: 3344, 2500, 1674, 1064 cm^{-1}. HRMS (*m/z*): calcd for $[C_6H_{16}N]^+$ 102.12773, obsd 102.12764; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd. 141.20542. ICP: calcd for B, 31.04%; found 30.05%.

7.4. Triaminoguanidinium hydrochloride (**11d**) [33]

A 250 mL R.B. flask was fitted with a magnetic stirrer and charged with 1,4-dioxane (100 mL). Ground guanidinium hydrochloride (**11a**, 19 g, 0.2 mol) was added in small portions to magnetically stirred dioxane to give a slurry. Then hydrazine monohydrate (34 mL, 32.7 g, 0.65 mol) was added to the slurry with vigorous stirring. During the addition, a clear solution was obtained, which was then heated to reflux. Shortly after the temperature reached 80 °C, a white precipitate began forming. The reaction was heated for an additional 2 h and allowed to cool to room temperature. The precipitate was filtered off, washed with dioxane, and air dried. The white product was recrystallized from hot water to give shiny white crystals of **11d** (26.5 g, 0.19 mol) in a 95% yield. The product was identified by its spectral data.

^{1}H NMR (DMSO): δ 8.59 (bs, 6H, NNH2), 4.50 (bs, 3H, NH) ppm. ^{13}C NMR (DMSO): δ 158.96 ppm. ^{13}C NMR (D$_2$O): δ 161.01 ppm. ESI-MS (*m/z*): 105.08887 ($CH_9N_6^+$, 100%). Anal. calcd for CH_9ClN_6 C, 8.54%; H, 6.45%; Cl, 25.22%; N, 59.78%, found: C, 8.46%; H, 6.54%; N, 59.21%.

7.5. Bis(guanidinium)dodecahydroborate dihydrate (*12a*)

A 250 mL Erlenmeyer flask was fitted with a magnetic stirrer and charged with 40 mL of aqueous Ag_2SO_4 solution (0.320 g, 1 mmol). Guanidinium hydrochloride (0.2 g, 2 mmol) was added to the Erlenmeyer with a spatula in small portions with vigorous stirring. Almost immediately, a white solid precipitated. The reaction mixture was stirred for 30 min and the precipitated AgCl was filtered and washed with a little water. The mother liquid was returned to the Erlenmeyer flask, $BaB_{12}H_{12}\cdot 4H_2O$ (0.353 g, 1 mmol) was added to the flask in small portions with stirring, and a white solid precipitated almost immediately. The mixture was stirred for an additional 30 min and the precipitated $BaSO_4$ was filtered off. The water was evaporated and a white solid was obtained, which was vacuum dried (0.250 g, 0.075 mol, 75% yield) and identified as the desired dodecahydroborate **12a**.

^{1}H NMR (DMSO-*d*$_6$): δ 6.91 (s, 12H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-*d*$_6$): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ 157.77 ppm. FTIR: 3577, 3491, 3347, 2500, 1634, 1065, 715 cm^{-1}. HRMS (*m/z*): calcd for $[CH_6N_3]^+$ 60.05562, obsd 60.05562; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.20560. ICP: calcd for B, 44.59%; found 44.00%.

7.6. Bis(aminoguanidinium)dodecahydroborate (*12b*)

A 25 mL R.B. flask was fitted with a magnetic stirrer and charged with distilled water (3 mL). Aminoguanidinium hydrochloride (**11a**, 0.112 g, 1.1 mmol) was added in small portions with stirring and a clear solution was obtained. Then $Na_2B_{12}H_{12}\cdot 4H_2O$ [8] (0.158 g, 0.6 mmol) was added to the flask in small portions with stirring. The solution became cloudy and a white voluminous precipitate formed. The stirring continued for a further 45 min and the reaction vessel was stored in the refrigerator (+4 °C) overnight. The solid was then vacuum filtered and dried in a desiccator to give the desired product in 73% yield (0.117 g, 0.4 mmol).

^{1}H NMR (DMSO-*d*$_6$): δ 8.56 (s, 2H), 7.21 (s, 4H), 6.76 (s, 4H), 4.68 (s, 4H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-*d*$_6$): δ −15.53 (d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ 158.62 ppm. FTIR: 3442, 3342, 2500, 1650, 1063, 716 cm^{-1}. HRMS (*m/z*): calcd $[CH_7N_4]^+$ 75.06652, obsd 75.06641; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.20561. ICP: calcd for B, 44.89%; found: B, 44.55%.

7.7. Bis(diaminoguanidinium)dodecahydroborate dihydrate (*12c*)

Compound **12c** was synthesized from diaminoguanidinium hydrochloride (**11b**, 0.136 g, 1.1 mmol) and $K_2B_{12}H_{12}$ (0.110 g, 0.5 mmol) using a similar procedure described for compound **12b**. The desired product was obtained as a white solid in 80% yield (0.128 g, 0.4 mmol).

^{1}H NMR (DMSO-*d*$_6$): δ 8.53 (s, 4H), 7.13 (s, 4H), 4.58 (s, 8H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-*d*$_6$): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ 159.60 ppm. FTIR: 3438, 3321,2500, 1668, 1065, 889 cm^{-1}. HRMS: calcd for $[CH_8N_5]^+$ 90.07742, obsd 90.07741; calcd for $[B_{12}H_{11}]^-$ 141.*20556*, obsd 141.20563. ICP: calcd for B, 36.87%; found 36.07%.

7.8. Bis(triaminoguanidinium)dodecahydroborate monohydrate (*12d*)

Compound **12d** was synthesized from triaminoguanidinium hydrochloride (**11c**, 0.154 g, 1.1 mmol) and $Na_2B_{12}H_{12}\cdot 4H_2O$ (0.158 g, 0.6 mmol) using a procedure similar to that described for compound **12b**. The desired product was obtained as a white solid in 73% yield (0.134 g, 0.4 mmol). M.p. 223 °C. The title compound was also prepared on a 1 g scale from triaminoguanidinium hydrochloride (1.26 g, 9 mmol) and $K_2B_{12}H_{12}$ (1 g, 4.50 mmol) in 20 mL distilled water using a similar procedure. The desired product was obtained as a white solid in 80% yield (1.26 g, 3.6 mmol). We have also succeeded in scaling up the preparation of **12d** to a 6 g scale, using a similar procedure, with little difficulty and commercial quantities should be feasible.

^{1}H NMR (DMSO-*d*$_6$): δ 8.59 (s, 6H), 4.48 (s, 12H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-*d*$_6$): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ 158.92 ppm. FTIR: 3318, 2500, 1674, 1061, 950 cm^{-1}. HRMS (*m/z*): calcd for $[CH_9N_6]^+$ 105.08835, obsd 105.08832; calcd for $[B_{12}H_{11}]^-$, 141.*20556*, obsd 141.20561. ICP: calcd for B, 35.48%; found 35.40%.

7.9. Bis(N-guanyluronium)dodecahydroborate (*12e*)

Compound **12e** was synthesized from N-guanylurea hydrochloride [34] (**11e**, 0.140 g, 1 mmol) and $K_2B_{12}H_{12}$ (0.110 g, 0.5 mmol) using a similar procedure described for compound **12b**. The desired product was obtained as a white solid in 80% yield (0.140 g, 0.4 mmol).

^{1}H NMR (DMSO-*d*$_6$): δ 10.11 (s, 2H), 8.14 (s, 8H), 7.19 (s, 4H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-*d*$_6$): δ −15.53 ppm (d, J_{BH} = 125 Hz). ^{13}C NMR (DMSO-*d*$_6$): δ 155.42, 154.34 ppm. FTIR: 3445, 3389, 3352, 3188, 2484, 1680, 1580, 1069, 702 cm^{-1}. HRMS (*m/z*): calcd for $[C_2H_7N_4O]^+$ 103.06144, obsd 103.06144; calcd for $[B_{12}H_{11}]^-$ 141.*20556*, obsd 141.20572. ICP: calcd for B, 37.71%; found 38.10%.

7.10. 1,5-Damino-4-methyltetrazolium iodide (*14*) [36,37]

A 50 mL R.B. flask was fitted with a magnetic stirrer and charged with 20 mL of dry acetonitrile and 1,5-diaminotetrazole [36,37] (**13**, 0.5 g, 5 mmol). Methyl iodide (2.84 g, 1.25 mL, 20. mmol) was added with stirring to the resulting suspension, and the flask was fitted with a reflux condenser. The entire apparatus was flushed with argon and remained under an argon atmosphere during the reaction. The flask was then immersed in an oil bath and heated to 70 °C overnight. The liquid was evaporated and light yellow solid was obtained. Then diethyl ether was added and the solid was vacuum filtered and dried in a desiccator to give the desired product **14** (0.930 g, 3.8 mmol, 77% yield).

^{1}H NMR (DMSO-*d*$_6$): δ 8.98 (s, 2H, N–NH$_2$), 7.09 (s, 2H, C–NH$_2$), 3.34(s, 3H, CH$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 147.73, 34.50. *Anal.* Calc. for $C_2H_7N_6I$ C, 9.93%; H, 2.92%; N, 34.72%; found: C, 9.88%; H, 3.03%; N, 35.30%.

7.11. Bis(1,4-dimethyl-5-aminotetrazolium)dodecahydroborate monohydrate (*15a*)

A 25 mL R.B. flask fitted with a magnetic stirrer was charged with distilled water (4 mL). 1,4-Dimethyl-5-aminotetrazolium iodide (**20a**, 0.320 g, 1.3 mmol) was added in small portions with stirring and a clear solution was obtained. Then $K_2B_{12}H_{12}$

(0.150 g, 0.6 mmol) was added to the flask in small portions with stirring. The solution became cloudy and a voluminous white precipitate formed. The stirring was continued for an additional 45 minutes and was stored in the refrigerator (+4 °C) overnight. The solid was vacuum filtered and dried in a desiccator, yielding the desired borate salt **15a** (0.140 g, 0.4 mmol, 66% yield). Compound **15a** was also prepared in 1 g scale from 1,4-dimethyl-5-aminotetrazolium iodide (**20a**, 1.28 g, 5.3 mmol) and $K_2B_{12}H_{12}$ (0.60 g, 2.64 mmol) in 12 mL distilled water using a similar procedure. The desired product was obtained as a white solid in 75% yield (0.730 g, 1.95 mmol).

^{1}H NMR (DMSO-d_6): δ 9.09 (s, 4H), 3.86 (s, 12H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 148.34, 33.91 ppm. FTIR: 3531, 3444, 2500, 1672, 1064, 704 cm^{-1}. HRMS (*m/z*): calcd for $[C_3H_8N_5]^+$ 114.07742, obsd 114.07748; calcd for $[B_{12}H_{11}]^-$ 141.20919, obsd 141.20917. ICP: calcd for B, 33.84%; found 33.45%.

*7.12. Bis(1-methyl-5-aminotetrazolium)dodecahydroborate monohydrate (**15b**)*

Compound **15b** was synthesized from 1-methy-5-aminotetrazolium chloride monohydrate (**20b**, 0.300 g, 2 mmol), 40 mL of Ag_2SO_4 solution (0.320 g, 1 mmol) and $BaB_{12}H_{12}\cdot 4H_2O$ (0.353 g, 1 mmol) using a procedure similar to that described for compound **15c** (Path D). The desired product was obtained as a white solid (0.250 g, 0.7 mmol, 73% yield).

^{1}H NMR (DMSO-d_6): δ 5.37 (s, 6H), 3.69 (s, 6H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 155.39, 31.47 ppm. FTIR: 3358, 3390, 3314, 3203, 2477, 1700, 1038, 712 cm^{-1}. HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ 100.06177, obsd 100.06210; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd. 141.20592. ICP: calcd for B, 36.60%; found: 36.90%.

*7.13. Bis(5-aminotetrazolium)dodecahydroborate trihydrate (**15c**) [11,27]*

A 100 mL Erlenmeyer flask was fitted with a magnetic stirrer and charged with 40 mL of an aqueous Ag_2SO_4 solution (0.320 g, 1 mmol). 5-Aminotetrazolium chloride monohydrate (0.30 g, 2 mmol) was added with a spatula in small portions with vigorous stirring. Almost immediately a white solid precipitated. The reaction mixture was stirred for 30 minutes and the precipitate (AgCl) was filtered and washed with a little water. Then, the mother liquid was returned to the Erlenmeyer flask and $BaB_{12}H_{12}\cdot 4H_2O$ (0.353 g, 1 mmol) was added to the flask in small portions with stirring. Almost immediately a white solid precipitated. The mixture was stirred for another 30 minutes and the precipitate ($BaSO_4$) was removed. The water was evaporated and a white solid was obtained, which was vacuum dried and recrystallized from acetonitrile. The product proved to be the desired borate salt **15c** (0.250 g, 0.8 mmol, 79% yield).

^{1}H NMR (DMSO-d_6): δ 6.30 (s, 6H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 155.71 ppm. FTIR: 3562, 3425, 3334, 3202, 2500, 1700, 1046, 715 cm^{-1}. HRMS (*m/z*) calcd for [$CH_4N_5^+$] 86. 0461, obsd 86.04653; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.20577. ICP: calcd for B, 35.67%; found 35.60%.

*7.14. Bis(1,5-diamino-4-methyltetrazolium)dodecahydroborate trihydrate (**15d**)*

Compound **15d** was synthesized from 1,5-diamino-4-methyltetrazolium iodide monohydrate (**14**, 0.290 g, 1.20 mmol), 40 mL of Ag_2SO_4 solution (0.192 g, 0.6 mmol) and $BaB_{12}H_{12}\cdot 4H_2O$ (0.168 g, 0.6 mmol) using a procedure similar to that described for compound **15c** (Path D). The desired product was obtained as a white solid (0.150 g, 0.4 mmol, 70% yield).

^{1}H NMR (DMSO-d_6): δ 8.89 (br s, 4H, N–NH_2), 6.97(s, 4H, C-NH_2), 3.78 (s, 6H, CH_3), 1.50–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.71 (d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 147.42, 34.28 ppm. MS (LCMS ESI$^+$): *m/z* 115.07249 ($C_2H_7N_6^+$, 100%). MS (LCMS ESI$^-$): *m/z* 141.20577($B_{12}H_{11}^-$, 58%), 165.20315 ($B_{12}H_{12}Na^-$, 100%). HRMS (*m/z*): calcd for $[C_3H_8N_5]^+$ 115.07267, obsd 115.07293; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.205770. ICP: calcd for B, 30.98% ; found 31.18%.

*7.15. Bis(1,3-dimethyl-5-aminotetrazolium)dodecahydroborate monohydrate (**16a**)*

Compound **16a** was synthesized from 1,3-dimethyl-5-aminotetrazolium iodide (**21a**, 0.320 g, 1.3 mmol) and $K_2B_{12}H_{12}$ (0.150 g, 0.6 mmol) using a procedure similar to that described for compound **15a** (Path C). The desired product was obtained as a white solid (0.167 g, 0.4 mmol, 66% yield).

^{1}H NMR (DMSO-d_6): δ 8.28 (s, 4H), 4.36 (s, 12H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 157.99, 42.50, 34.13 ppm. FTIR: 3425, 3335, 2500, 1652, 1062, 720 cm^{-1}. HRMS (*m/z*): calcd for $[C_3H_8N_5]^+$ 114.07742, obsd 114.07748; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.205770. ICP: calcd for B, 33.88%; found: 33.33%.

*7.16. Bis(2-methyl-5-aminotetrazolium)dodecahydroborate dihydrate (**16b**)*

Compound **16b** was synthesized from 2-methy-5-aminotetrazolium chloride monohydrate (**21b**, 0.300 g, 2 mmol), 40 mL of Ag_2SO_4 solution (0.320 g, 1 mmol) and $BaB_{12}H_{12}\cdot 4H_2O$ (0.353 g, 1 mmol) using a procedure similar to that described for compound **15c** (Path D). The desired product was obtained as a white solid (0.240 g, 0.7 mmol, 70% yield).

^{1}H NMR (DMSO-d_6): δ 4.58 (s, 6H), 4.06 (s, 6H), 1.60–0.30 (br m, 12H) ppm. ^{11}B NMR (DMSO-d_6): δ −15.53(d, J_{BH} = 125 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 167.04, 38.70 ppm. FTIR: 3565, 3424, 3335, 3203, 2500, 1699, 1623, 1064, 715 cm^{-1}. MS (TOF ES$^+$): *m/z* 100.06208 (M$^+$, 100%). MS (TOF ES$^-$): *m/z* 141.20772 ($B_{12}H_{11}^-$, 39.52%), 165.20325 ($B_{12}H_{12}Na^-$, 100%). HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ 100.06177, obsd 100.06209; calcd for $[B_{12}H_{11}]^-$ 141.20556, obsd 141.20919. ICP: calcd for B, 34.92%; found 34.70%.

*7.17. 1-Methyl-5-aminotetrazole (18) and 2-Methyl-5-aminotetrazole (**19**) [38,40]*

A 500 mL R.B. flask was fitted with a magnetic stirrer and charged with 30 mL of distilled water and 5-aminotetrazole monohydrate (**17**, 10.3 g, 0.1 mol), which formed a suspension. The flask was fitted with a pressure equalizing addition funnel containing 25 mL of 20% NaOH solution (5 g, 0.125 mol). The solution was added dropwise to the flask over 0.5 h. A clear solution was obtained in the flask. Then the pressure equalizing addition funnel was replaced by another pressure equalizing addition funnel containing a solution of methyl iodide (14.2 g, 6.22 mL, 0.1 mol) in 160 mL of acetone. The methyl iodide solution was added dropwise to the flask over an hour. Afterwords, the reaction solution was stirred at room temperature for three days and monitored by tlc as it proceeded to completion. During this 72 h period most of the acetone evaporated. The reaction solution was transferred to 500 mL beaker and left in the hood overnight. A white solid precipitated (6.6 g), which was spectroscopically identified as 95:5 mixture of 1-methyl-5-aminotetrazole (**18**) and 2-methyl-5-aminotetrazole (**19**). This mixture was recrystallized from an acetone–water mixture yielding pure product **18** (5 g, 0.05 mol, 50% yield); m.p. 220 °C. TLC (acetonitrile) R_f = 0.65. The original mother liquor (from which the 6.6 g precipitated) was evaporated, and 150 mL chloroform was added to the remaining white solid (which contained the minor product **19** and the inorganic salt NaI). The slurry was magnetically stirred overnight in order to extract the organic material, and the solid sodium iodide was filtered off. The yellow chloroform was evaporated yielding the desired product **19**. The latter was obtained pure via recrystallization from water (1.8 g, 0.018 mol, 18% yield); M.p. 105 °C. TLC (acetonitrile): R_f = 0.55.

18: ^{1}H NMR (DMSO-d6): δ 6.66 (s, 2H), 3.70 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 155.71, 32.03 ppm. HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ 100.06185, obsd 100.06177.

19: ^{1}H NMR (DMSO-d6): δ 5.96 (s, 2H), 4.07(s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 167.05, 38.68 ppm. HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ 100.06181, obsd 100.06177.

*7.18. 1,4-Dimethyl-5-aminotetrazolium iodide (**20a**) [38]*

A 250 mL R.B. flask was fitted with a magnetic stirrer and charged with 60 mL of acetonitrile and 1-methyl-5-aminotetrazole (**18**, 4 g, 40 mmol). Methyl iodide (10 mL, 0.16 mol) was added with stirring to the resulting suspension, and the flask was fitted with a reflux condenser. The entire apparatus was flushed with argon and remained under an argon atmosphere during the reaction. The flask was then immersed in an oil bath and heated to reflux overnight. The liquid was carefully concentrated in the evaporator until slight turbidity was observed and left aside for crystallization. The white solid obtained was vacuum filtered and dried in a desiccator to give the desired product **20a** (6.5 g, 30 mmol, 75% yield) m.p. 220 °C.

^{1}H NMR (DMSO-d_6): δ 9.10 (s, 2H), 3.87 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6): δ 148.40, 34.04 ppm. FTIR: 3247, 3088, 1679, 1453, 1051, 785, 688 cm^{-1}. HRMS (*m/z*): calcd for $[C_3H_8N_5]^+$ 114.07742, obsd 114.07746; calcd for $[I]^-$ 126.90502, obsd 126.90481.

*7.19. 1-Methyl-5-aminotetrazolium chloride monohydrate (**20b**)*

Compound **20b** was synthesized from 1-methyl-5-aminotetrazole (**18**, 1 g, 10 mmol) and HCl (37%, 5 mL, 0.06 mol) using a procedure similar to that described for compound **20c**. The desired product was obtained as a white solid (0.8 g, 5 mmol, 50% yield), m.p. 207 °C.

^{1}H NMR (DMSO-d_6): δ 8.27 (s, 5H), 3.78 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 155.10, 31.54. FTIR: 3247, 3078, 2565, 2362, 1650, 1272, 1033, 970, 822, 780, 713 cm^{-1}.

*7.20. 1-Methyl-5-aminotetrazolium sulfate (**20b**-sulfate)*

A *50* mL Erlenmeyer flask was fitted with a magnetic stirrer and charged with *30* mL of distilled water. 1-Methyl-5-aminotetrazole (**18**, *2* g, *20* mmol) was added with stirring and heated to 40 °C until a clear light green solution was obtained. H_2SO_4 (98%, 1 g, 10 mmol) was carefully added with stirring. The water solution was cooled to room temperature, transferred to a 100 mL R.B. flask and rotary evaporated to dryness. The residual pale yellow solid was recrystallized from hot water and a white solid was obtained. The isolated product was identified as **20b-sulfate** (1.1 g, 3.4 mmol, 34% yield). m.p. 225 °C.

^{1}H NMR (DMSO-d_6): δ 8.17(s,3H), 3.72(s,3H). ^{13}C NMR (DMSO-d_6): δ 154.80, 31.61. FTIR: 3675, 3322, 3150, 2989, 2900, 1662, 1592, 1405, 1066, 789, 693 cm^{-1}. HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ *100*.06177, obsd *100*.006211; calcd for $[HO_4S]^-$ 96.96010, obsd. 96.96034.

*7.21. 5-Aminotetrazolium chloride monohydrate (**20c**) [41]*

A 100 mL R.B. flask fitted with a magnetic stirrer and a reflux condenser, was charged with 20 mL of methanol and 5-aminotetrazole monohydrate (**17**, 1 g, 0.01 mol). HCl (37%, 5 mL, 0.06 mol) was added with stirring to the resulting suspension. The reaction flask was immersed into an oil bath and heated under reflux overnight. The solvent was evaporated and the residual white solid was recrystallized from a minimal amount of methanol to which ether was added (0.8 g, 6 mmol, 60% yield), m.p. 185 °C.

^{1}H NMR (DMSO-d_6): δ 8.05 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 155.18, FTIR: 3347, 3094, 2645, 2362, 1650, 1287, 1063, 774, 705 cm^{-1}.

*7.22. Aminotetrazolium sulfate dihydrate (**20c-sulfate**) [39]*

A 50 mL Erlenmeyer flask was fitted with a magnetic stirrer and charged with 20 mL of distilled water. 5-Aminotetrazole monohydrate (**17**, 2 g, 20 mmol) was added to the flask with stirring and heated to 40 °C until a clear solution was obtained. H_2SO_4 (98%, 1 g, 10 mmol) was then carefully added with stirring. The aqueous solution was cooled to room temperature, transferred to a 100 mL R.B. flask and rotary evaporated to dryness. The residual white solid was recrystallized from hot water. The isolated product was identified as **20c-sulfate** (2.7 g, 10 mmol, 100% yield), m.p. 193 °C.

^{1}H NMR (DMSO-d_6): δ 7.56 (s,4H). ^{13}C NMR (DMSO-d_6): δ 155.88. FTIR: 3473, 3338, 1600, 1449, 1297, 1156, 1050, 994, 902, 755 cm^{-1}. HRMS (*m/z*): calcd for $[CH_4N_5]^+$ 86.04610, obsd. 86.04650; calcd for $[HO_4S]^-$ 96.96020, obsd. 96.96010. ICP: calcd for S, 10.52%; Found 10.50%.

*7.23. 1, 3-Dimethyl-5-aminotetrazolium iodide (**21a**) [51]*

A 100 mL R.B. flask was fitted with a magnetic stirrer and charged with 20 mL of acetonitrile and 2-methyl-5-aminotetrazole (**19**, 1 g, 10 mmol). Methyl iodide (1.25 mL, 0.02 mol) was added with stirrig to the resulting suspension, and the flask was fitted with a reflux condenser. The entire apparatus was flushed with argon and remained under an argon atmosphere during the reaction. The flask was then immersed in an oil bath and heated to reflux overnight. The liquid was carefully concentrated in the evaporator until slight turbidity was formed and left aside for crystallization. A white solid was obtained The solid was then vacuum filtered and dried in a desiccator to give the desired product **21a** (1.70 g, 7.05 mmol, 71% yield); m.p. 190 °C.

^{1}H NMR (DMSO-d_6): δ 8.26 (s, 2H), 4.37 (s, 3H), 3.94 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 157.95, 42.60, 34.28 ppm. HRMS (*m/z*): calcd for $[C_3H_8N_5]^+$ 114.07742, obsd 114.07746; calcd for $[I]^-$ 126.90502, obsd 126.90481.

*7.24. 2-Methyl-5-aminotetrazolium chloride monohydrate (**21b**)*

Compound **21b** was synthesized from 2-methyl-5-aminotetrazole (**19**, 1 g, 10 mmol) and HCl (37%, 5 mL, 0.06 mol) using a procedure similar to that described for compound **20c**. The desired product was obtained as a white solid (0.3 g, 2 mmol, 30% yield), m.p. 95 °C.

^{1}H NMR (DMSO-d_6): δ 5.88 (s, 5H), 4.08 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 167.08, 38.70. FTIR: 325 1, 3216, 3086, 1660, 1536, 1453, 1185, 1051, 795 cm^{-1}.

*7.25. 2-Methyl-5-aminotetrazolium sulfate (**21b-sulfate**)*

A 50 mL Erlenmeyer flask was fitted with a magnetic stirrer and charged with 10 mL of distilled water. 2-Methyl-5-aminotetrazole (**19**, 0.85 g, 8.5 mmol) was added with stirring and immediately a clear solution was obtained. H_2SO_4 (98%, 0.4 g, 4 mmol) was carefully added with stirring. The water solution was transferred to a 100 mL R.B. flask and rotary evaporated to dryness. The residual slight yellow solid was recrystallized from hot water and a white solid was obtained. The isolated product was identified as **21b-sulfate** (1.1 g, 3.8 mmol, 90% yield), m.p. 97 °C.

^1H NMR (DMSO-d_6): δ 7.72 (s,3H), 4.08 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 167.01, 38.72. FTIR: 3367, 3216, 1671, 1631, 1549, 1408, 1203, 1050, 1015, 837, 755 cm^{-1}. HRMS (*m/z*): calcd for $[C_2H_6N_5]^+$ *100*.06177, obsd *100*.006202. calcd for $[HO_4S]^-$ 96.96030, obsd. 96.96010.

Acknowledgements

We would like to acknowledge the kind and generous support of the Israeli Ministry of Defense and the Ethel and David Resnick Chair in Active Oxygen Chemistry.

A. Supplementary data

CCDC 1856419 contains the supplementary crystallographic data for compound **12d** recrystallized from pure DMF, while CCDC 1856418 contains the same data for compound **12d** recrystallized from a DMF/NMP mixture. The crystallographic data for **15a** are contained in CCDC 1856508. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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