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closo-Hydroborates from Liquid Ammonia: Synthesis and Crystal Structures of $[Li(NH_3)_4]_2[B_{12}H_{12}]\cdot 2NH_3$, $Rb_2[B_{12}H_{12}]\cdot 8NH_3$, $Cs_2[B_{12}H_{12}]\cdot 6NH_3$ and $Rb_2[B_{10}H_{10}]\cdot 5NH_3$

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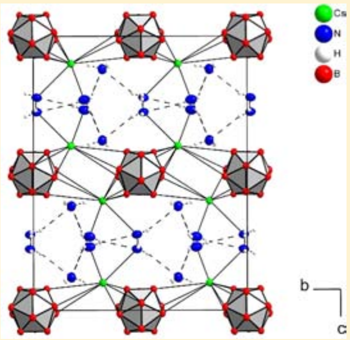
ABSTRACT: Ammonia complexes of hydroborates may be potentially promising materials for ammonia storage or indirect hydrogen storage. The title compounds contain 20.04–52.23 wt % ammonia and 5.94–13.01 wt % hydrogen. They were synthesized in liquid ammonia, using $(NBu_4)_2[B_{12}H_{12}]$ and $Li_2[B_{10}H_{10}]$ as starting materials. $[Li(NH_3)_4]_2[B_{12}H_{12}]\cdot 2NH_3$ (**1**) crystallizes in the monoclinic crystal system (space group $P2_1/c$, $a = 9.183(2)$ Å, $b = 8.133(1)$ Å, $c = 16.375$ Å, $\beta = 110.54(1)°$, $V = 1143.97(40)$ Å^3, $Z = 2$). The compound is a direct precursor of the hydrogen storage compound $Li_2[B_{12}H_{12}]\cdot 7NH_3$. Hydroborates of the heavier alkali metals were found to crystallize in the orthorhombic crystal system: $Rb_2[B_{12}H_{12}]\cdot 8NH_3$ (**2**) (space group *Pnnm*, $a = 14.4166(6)$ Å, $b = 7.8221(3)$ Å, $c = 9.5792(4)$ Å, $V = 1080.23(8)$ Å^3, $Z = 2$), $Cs_2[B_{12}H_{12}]\cdot 6NH_3$ (**3**) (space group *Pbca*, $a = 7.7569(8)$ Å, $b = 14.087(2)$ Å, $c = 18.075(2)$ Å, $V = 1974.99(30)$ Å^3, $Z = 4$), and $Rb_2[B_{10}H_{10}]\cdot 5NH_3$ (**4**) (space group *Pnma*, $a = 13.9510(7)$ Å, $b = 8.675(2)$ Å, $c = 13.966(2)$ Å, $V = 1690.2(3)$ Å^3, $Z = 4$), as determined by single crystal X-ray diffraction. The structures are discussed briefly.

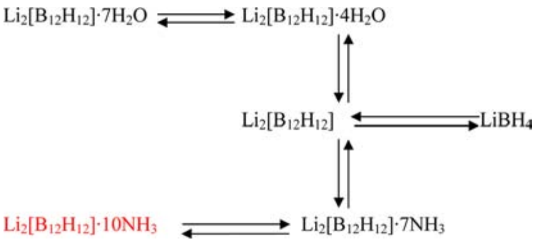


INTRODUCTION

Complex hydrides are broadly investigated in the context of hydrogen storage.[1] Hydroaluminates for example were found to be valuable materials in terms of the weight/capacity ratio,[2] and this certainly holds also for hydroborates, compounds that are furthermore known to be very interesting due to their fascinating structures and special bonding situations.[3−9] Only in 2005, the first hydroborate ammoniate synthesized in liquid ammonia was published.[8] Since then, ammine complexes like $Zn(BH_4)_2\cdot 2NH_3$,[10] $Mg(BH_4)_2\cdot 2NH_3$,[11] $Al(BH_4)_3\cdot 6NH_3$,[12] $Li_2Al(BH_4)_5\cdot 6NH_3$[13] and $Li_2B_{12}H_{12}\cdot 7NH_3$[14] have been discovered as promising materials. $Li_2[B_{12}H_{12}]\cdot 7NH_3$ is a room temperature stable compound obtained by reaction of $Li_2B_{12}H_{12}$ with ammonia,[14] and it was discussed for ammonia and indirect hydrogen storage.

Not many synthetic routes for hydroborates except for that of crystallization from water solutions were developed.[15,16] The synthesis of water-free lithium hydroborates is not a trivial task. The first successful synthesis procedure to obtain $Li_2B_{12}H_{12}$ in good yields was described in 1971 by Kuznetsov et al.[17] based on the reaction of $NaBH_4$ and $B_{10}H_{14}$. The primary product is $Na_2B_{12}H_{12}\cdot 4H_2O$ which can be easily transformed to the free acid $(H_3O)_2B_{12}H_{12}$ from which $Li_2B_{12}H_{12}\cdot xH_2O$ is obtained by a neutralization reaction with LiOH. The authors obtained a white product initially described as $Li_2B_{12}H_{12}\cdot 5H_2O$, however, crystal structure data was not reported. Later, single crystals of $Li_2[B_{12}H_{12}]\cdot 7H_2O$ were obtained from neutralization reaction of $(H_3O)_2[B_{12}H_{12}]$ with LiOH and slow evaporation of the water.[15] The heptahydrate could be converted to $Li_2[B_{12}H_{12}]\cdot 4H_2O$[18] and further dried in vacuo to yield anhydrous $Li_2[B_{12}H_{12}]$ (Scheme 1).[19,20] Züttel and co-workers have shown that anhydrous $Li_2[B_{12}H_{12}]$ can also be obtained from the reaction of $LiBH_4$.[21] $Li_2[B_{12}H_{12}]$ was discussed as an intermediate in the thermal decomposition of $LiBH_4$.[20,21]

Scheme 1. Various Routes for the Synthesis of Anhydrous $Li_2B_{12}H_{12}$[a]



[a]Black = known, red = this work.

We had earlier investigated the synthesis and crystal structure of alkali metal and alkylammonium *closo*-hydroborates with undistorted boron atom polyhedra,[3,4] in order to compare them with typical building units found in boron-rich borides.[22] Of the solvent-free alkali metal hydroborates, only $M_2B_6H_6$ (M = K, Cs), $Rb_2B_9H_9$ and $M_2B_{12}H_{12}$ (M = K, Rb, Cs) have been

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Table 1. Crystal Data and Structure Refinement for Compounds 1−4

	1	2	3	4
empirical formula	$H_{42}B_{12}Li_2N_{10}$	$H_{36}B_{12}N_8Rb_2$	$H_{30}B_{12}Cs_2N_6$	$H_{25}B_{10}N_5Rb_2$
formula mass/g mol^{-1}	326.04	449.03	509.84	374.29
wavelength/Å	0.71073	0.71073	0.71073	0.71073
temp/K	123(2)	123(2)	123(2)	123(2)
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group (No.)	$P2_1/c$ (14)	*Pnnm* (58)	*Pbca* (61)	*Pnma* (62)
a/Å	9.183(2)	14.4166(6)	7.7569(8)	13.9510(7)
b/Å	8.133(1)	7.8221(3)	14.087(2)	8.675(1)
c/Å	16.357(3)	9.5792(4)	18.075(2)	13.966(1)
α/deg	90	90	90	90
β/deg	110.54(1)	90	90	90
γ/deg	90	90	90	90
V/Å^3	1144.0(4)	1080.23(8)	1975.0(3)	1690.2(3)
Z	2	2	4	4
ρ_c/Mg m^{-}	0.947	1.381	1.715	1.471
μ(Mo Kα)/mm^{-1}	0.054	4.528	3.681	5.770
F(000)	356	452	968	736
θ range for data collection [deg]	2.37−28.04	2.55−32.50	2.25−28.12	2.06−27.50
reflns collected	13396	27899	22433	37094
indep reflns	2696	2053	2386	2072
reflns with $I > 2\sigma(I)$	1258	1520	1792	1368
R_{int}	0.0691	0.0632	0.0465	0.1405
θ_{max} [deg]	28.04	32.50	28.12	27.50
data/restraints/params	2696/0/193	2053/0/97	2386/0/151	2072/0/145
goodness-of-fit on F^2	0.714	0.953	0.868	0.805
$R(F)$ (all data)	0.0907	0.0307	0.0279	0.0489
wR(F^2) (all data)	0.0746	0.0448	0.0347	0.0472
$w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, $P = (F_o^2 + 2F_c^2)/3$	$a = 0.0285$, $b = 0$	$a = 0.0231$, $b = 0$	$a = 0.0140$, $b = 0$	$a = 0.0143$, $b = 0$
$(\Delta/\sigma)_{max}$	0.001	0.000	0.002	0.000
$\Delta\rho_{max}$ [e Å^{-3}]	0.199	0.672[a]	0.780[a]	0.613[a]
$\Delta\rho_{min}$ [e Å^{-3}]	−0.209	−0.286	−0.314	−0.311

[a]Within 1 Å around the heavy atom.

structurally characterized in the solid state.[23−27] Lately, $Na_2B_{10}H_{10}$, $K_2B_{10}H_{10}$ and $Rb_2B_{10}H_{10}$ were obtained as crystalline powders and their structures could be solved ab initio from powder data.[5,6] Until recently,[8] NH_3 has only been used as a Lewis base in reactions with boranes, or for the formation of boronitrides or borazanes.[28−33] As a consequence, our first step was to crystallize alkylammonium, ammonium, alkali metal or alkali earth metal hydroborates as ammoniates. A gentle removal of NH_3 may lead to the formation of novel solvent-free, crystalline hydroborates or new solvent-free modifications of known compounds which might become important for ammonia or hydrogen storage.

We were able to obtain the novel anhydrous hydroborates **1** to **4** from syntheses in liquid ammonia, and we discuss their synthesis and crystal structures. The discussion of the obtained crystal structures of compounds **1** to **4** is highly interesting in the context of the binding situation of electron deficient compounds.[3−7,9]

■ EXPERIMENTAL SECTION

Materials and Methods. All work was done excluding moisture and air in an atmosphere of purified argon. $(NBu_4)_2(B_{12}H_{12})$ was obtained from Prof. Dr. Gabel, University of Bremen. $Li_2B_{10}H_{10}$ was synthesized according to procedures described in the literature.[34] Both hydroborates were dried in vacuo prior usage. Liquid ammonia was dried and stored over sodium at −78 °C; methods for liquid ammonia chemistry are available from the literature.[35−37] Alkali metals were distilled prior to use and stored in flame-sealed glass ampules under argon.[38]

Preparation of $[Li(NH_3)_4]_2[B_{12}H_{12}]\cdot 2NH_3$ (1). A reaction vessel was charged with 0.017 g (2.45 mmol) of distilled lithium, 0.313 g (0.50 mmol) of $(NBu_4)_2[B_{12}H_{12}]$ and 15 mL of ammonia at −78 °C. After storage for ten days at −38 °C, colorless cube-shaped crystals were obtained in quantitative yield by decantation of the dissolved excess Li and $(NBu_4)NH_2$. The crystals of **1** decompose under liberation of ammonia upon warming to room temperature to yield $Li_2[B_{12}H_{12}]\cdot 7NH_3$ as evidenced by X-ray powder diffraction. $Li_2[B_{12}H_{12}]\cdot 7NH_3$ dissolves again in liquid ammonia to form **1** upon crystallization.

Preparation of $Rb_2[B_{12}H_{12}]\cdot 8NH_3$ (2). A reaction vessel was charged with 0.572 g (6.69 mmol) of distilled rubidium, 0.839 g (1.34 mmol) of $(NBu_4)_2[B_{12}H_{12}]$ and 15 mL of ammonia at −78 °C. After storage for one month at −38 °C, colorless plate-shaped crystals of suitable size for X-ray structure analysis were obtained in quantitative yield by decantation of the dissolved excess Rb and $(NBu_4)NH_2$.

Preparation of $Cs_2[B_{12}H_{12}]\cdot 6NH_3$ (3). A reaction vessel was charged with 0.291 g (2.2 mmol) of distilled cesium, 0.274 g (0.44 mmol) of $(NBu_4)_2[B_{12}H_{12}]$ and 15 mL of ammonia at −78 °C. After storage for eight days at −38 °C, colorless plate-shaped crystals were obtained in quantitative yield by decantation of the dissolved excess Cs and $(NBu_4)NH_2$.

Preparation of $Rb_2[B_{10}H_{10}]\cdot 5NH_3$ (4). A reaction vessel was charged with 1.093 g (12.79 mmol) of distilled rubidium, 0.167 g (1.26 mmol) of $Li_2[B_{10}H_{10}]$, and 15 mL of ammonia at −78 °C. After storage for two weeks at −38 °C, colorless needle-shaped crystals of suitable size for low-temperature X-ray structure analysis were obtained by decantation of the dissolved excess Rb. As the crystals of **4** were immersed in insoluble $LiNH_2$, as evidenced by single crystal and powder X-ray diffraction, no yield could be determined.

X-ray Crystallographic Study. The single-crystal X-ray structure determinations (Table 1) were carried out on a Bruker Smart Apex CCD-diffractometer with graphite monochromator using Mo $K\alpha$ radiation $\lambda = 0.71073$ Å, a temperature of $T = 123(2)$ K and ω-scans.[39] Absorption correction was done using the program SADABS.[40] The structures were solved using Direct Methods (program package SHELXS97)[41] and refined on F^2 (program SHELXL97).[42] All H atoms were localized by Fourier cycling methods, and their displacement parameters were refined either isotropically or, in the case of the non-hydrogen atoms, anisotropically. To reassure the assignment of the proper space group, symmetry checks on non-hydrogen atoms using the programs PLATON and KPLOT were executed after the refinement had converged.[43,44] The structures were visualized using the program DIAMOND.[45]

Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-414142 for (**1**), CSD-414143 for (**2**), CSD-414144 for (**3**) and CSD-414145 for (**4**).

■ RESULTS AND DISCUSSION

Bis(tetraammine lithium) Dodecahydro-*closo*-dodecaborate Ammonia (1/2), $[Li(NH_3)_4]_2[B_{12}H_{12}]\cdot 2NH_3$. Lithium metal and $(NBu_4)_2[B_{12}H_{12}]$ react in liquid ammonia according to eq 1:

$$2Li + (NBu_4)_2[B_{12}H_{12}] + 12NH_3 \rightarrow [Li(NH_3)_4]_2[B_{12}H_{12}]\cdot 2NH_3 + H_2 + 2(NBu_4)NH_2 \quad (1)$$

Crystals of **1** were obtained by decantation of $(NBu_4)NH_2$ and subjected to X-ray structure analysis. All atoms are located on general positions (Wyckoff symbol 4*e*) of space group $P2_1/c$. The dodecahydro-*closo*-dodecaborate cage is built up by six boron and six hydrogen atoms and their symmetry equivalents, forming the well-known $B_{12}H_{12}{}^{2-}$ molecule, which is similar in shape to an icosahedron. The B–B bond lengths are observed in the typical range found for $[B_{12}H_{12}]^{2-}$ at approximately 1.77(1) Å.[3,25−27,46−48] B–H bond lengths are observed with 1.11(1) Å. The $[B_{12}H_{12}]^{2-}$ cage is surrounded by six symmetry equivalent tetraammine lithium ions with Li–B distances ranging from 4.23 Å to 4.88 Å. The Li cations surround the anion octahedron-like. As mentioned previously, the lithium cation is tetrahedron-like coordinated by four molecules of ammonia. To the latter another molecule of ammonia is attached via a N–H···N hydrogen bond leading to the formation of a $^1_\infty[Li(NH_3)_4\cdot NH_3]$ zigzag chain running along the *b*-axis shown in Figure 1 and Figure 2. These strands are separated by the $[B_{12}H_{12}]^{2-}$ cages, and the unit cell of **1** is shown in Figure 3. Warming crystals of this compound to room temperature leads to the liberation of ammonia and formation of $Li_2[B_{12}H_{12}]\cdot 7NH_3$ as evidenced by X-ray powder diffractometry. $Li_2[B_{12}H_{12}]\cdot 7NH_3$ dissolves in liquid ammonia and re-forms **1** on crystallization at −38 °C.

Tetra-μ-ammine Bis(diammine rubidium) Dodecahydro-*closo*-dodecaborate, $Rb_2B_{12}H_{12}\cdot 8NH_3$. Rb metal and $(NBu_4)_2[B_{12}H_{12}]$ react in liquid ammonia solution according to eq 2:

$$2Rb + (NBu_4)_2[B_{12}H_{12}] + 10NH_3 \rightarrow Rb_2[B_{12}H_{12}]\cdot 8NH_3 + H_2 + 2(NBu_4)NH_2 \quad (2)$$

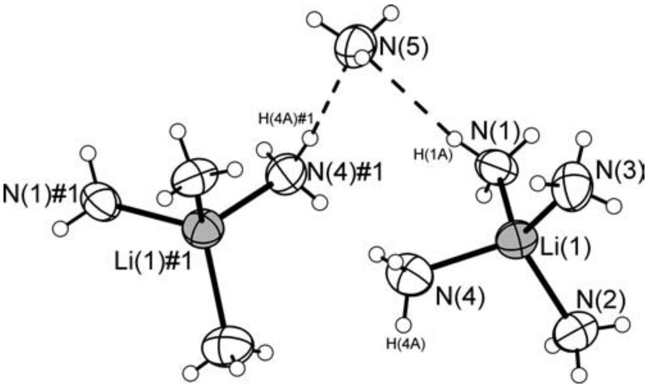

Figure 1. Fragment of the $^1_\infty[Li(NH_3)_4\cdot NH_3]$ zigzag chain. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Selected hydrogen bond lengths [Å] and angles [deg]: N(1)–H(1A) 0.90(2), N(5)···H(1A) 2.55, ∠N(1)–H(1A)···N(5) 165.9, N(4)#1–H(4A)#1 0.89(2), N(5)···H(4A)#1 2.32, ∠N(4)#1–H(4A)#1···N(5) 170.5. Symmetry transformations to generate equivalent atoms: #1 $-x + 1, y + 0.5, -z + 0.5$.

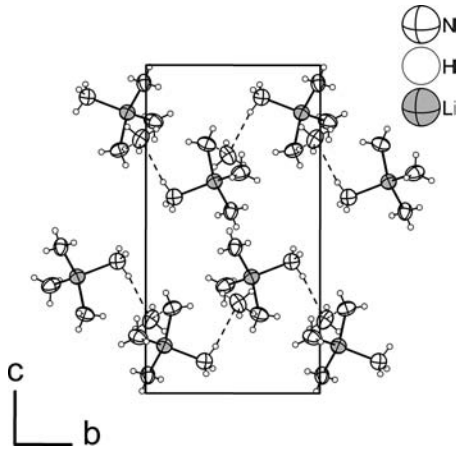

Figure 2. Projection of the $^1_\infty[Li(NH_3)_4]$ chains onto the *bc*-plane. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K.

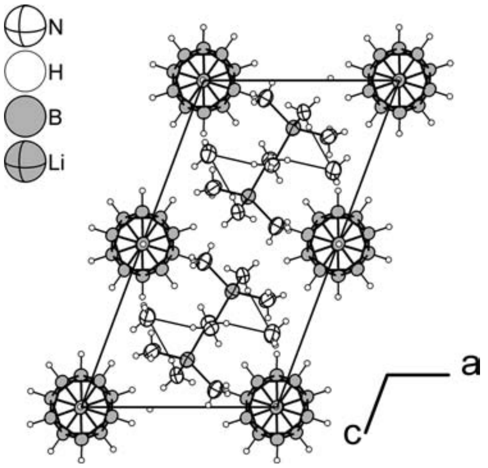

Figure 3. Projection on the *ac*-plane showing the $^1_\infty[Li(NH_3)_4]$ strands which are separated by the $B_{12}H_{12}{}^{2-}$ cages. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K.

Colorless crystals of **2** were obtained by decanting the dissolved $(NBu_4)_2NH_2$ and analyzed by single crystal X-ray diffraction. The $B_{12}H_{12}^{2-}$ cage is built up by only four boron and hydrogen atoms. Two atoms of each kind are situated on the special 4*g* position, the others on the general 8*h* position of space group *Pnnm*. Boron−boron and boron−hydrogen bond lengths are again in the typical range for the $B_{12}H_{12}^{2-}$ anion, varying around 1.78 Å and about 1.1 Å respectively. The $B_{12}H_{12}^{2-}$ anion is coordinated by four symmetry equivalent rubidium atoms with Rb−H distances of approximately 3.17 Å, 3.06 Å and 3.19 Å (Figure 4). The rubidium ion coordinates η^3-like to the *closo*-hydroborate cage and is surrounded by six partly symmetry equivalent ammonia molecules yielding a coordination number of nine for rubidium (Figure 5). Furthermore the ammonia molecules N(2) and N(3) and their symmetry equivalents, respectively, act as bridging ligands from rubidium to its symmetry equivalent forming a tetra-μ-ammine−bis(diamminerubidium) complex shown in Figure 6. The packing of the $B_{12}H_{12}^{2-}$ and $[Rb_2(NH_3)_8]^{2+}$ units corresponds to two body-centered lattices put together, which results in the formation of $[Rb_2(NH_3)_8]^{2+}$-$[B_{12}H_{12}]^{2-}$ layers in the *bc*-plane. Figure 7 shows the unit cell of **2**. Upon warming **2** to room temperature ammonia gas is liberated, and the resulting phase and its ammonia storage properties will be discussed elsewhere.

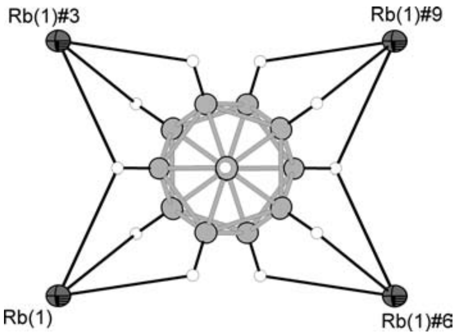

Figure 4. Coordination sphere of the $B_{12}H_{12}^{2-}$ anion. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Symmetry transformations to generate equivalent atoms: #2 $-x, -y, z$; #3 $-x, -y, -z + 1$; #6 $x, y + 1, z$; #9 $-x, -y + 1, -z + 1$.

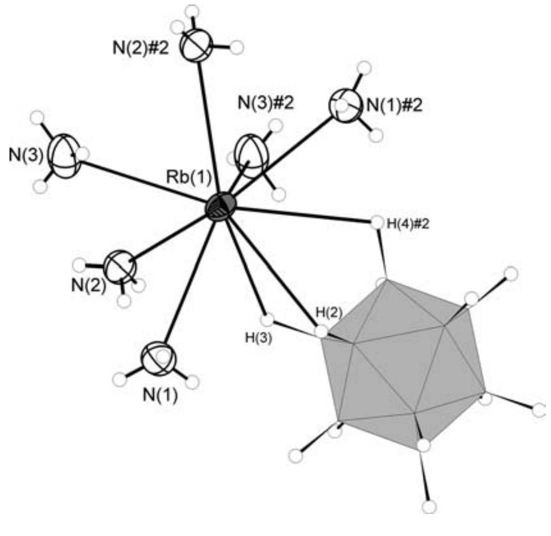

Figure 5. Coordination sphere of the rubidium ion. Boron atoms of the $B_{12}H_{12}^{2-}$ anion are shown as a polyhedron. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Selected bond lengths [Å]: Rb(1)−N(1) 3.176(1), Rb(1)−N(2) 3.132(1), 3.230(1). Symmetry transformations to generate equivalent atoms: #2 $-x, -y, z$.

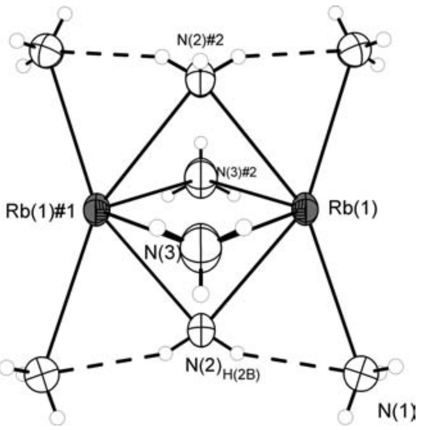

Figure 6. Perspective view of the μ_2-like bridging of the symmetry equivalent Rb ions via the nitrogen atoms N(2) and N(3). Dashes show N−H···N hydrogen bonding; selected bond length [Å] and angles [deg]: N(2)−H(2B) 0.834(1), N(1)···H(2B) 2.45, ∠N(2)−H(2B)···N(1) 155. Symmetry transformations to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y, z$.

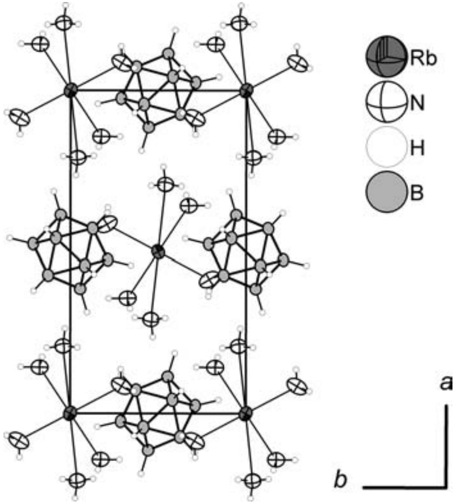

Figure 7. Projection on the *ab*-plane. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Shown is the stacking of $[Rb_2(NH_3)_8][B_{12}H_{12}]$ layers along the *a*-axis.

Dicesium Dodecahydro-*closo*-dodecaborate Ammonia (1/6), $Cs_2B_{12}H_{12}\cdot 6NH_3$.

Cs metal and $(NBu_4)_2[B_{12}H_{12}]$ react in liquid ammonia solution according to eq 3:

$$2Cs + (NBu_4)_2[B_{12}H_{12}] + 8NH_3 \rightarrow Cs_2[B_{12}H_{12}]\cdot 6NH_3 + H_2 + 2(NBu_4)NH_2 \quad (3)$$

Colorless crystals of **3** were obtained by decanting the dissolved $(NBu_4)_2NH_2$ and analyzed by single crystal X-ray diffraction. All atoms of **3** reside on the general 8*c* position of space group *Pbca* with one cesium atom, three nitrogen, six boron and fifteen hydrogen atoms in the asymmetric unit. By symmetry a $B_{12}H_{12}^{2-}$ cage and six ammonia molecules are generated. All B−B bonds are observed at about 1.76 Å; the B−H bonds are approximately 1.1 Å long. The $B_{12}H_{12}^{2-}$ anion is surrounded by six symmetry equivalent cesium cations with Cs−H distances between 3.00 Å and 3.48 Å as shown in Figure 8. The cesium ion coordinates η^3- and η^2-like to three symmetry equivalent *closo*-hydroborate cages and to two ammonia molecules N(2) and N(3) with bond lengths of 3.259(2) Å and 3.125(2) Å respectively (see Figure 9), yielding a coordination number of ten. Two ammonia molecules not only coordinate to Cs but also form N−H···N hydrogen bonds to N(1) and its symmetry equivalents. N(1) is acting as an acceptor of three hydrogen bonds, two from the symmetry equivalents of N(3) via H(3A) and H(3B) and one from the symmetry equivalents of N(2) via H(2A). N(3) is forming a third hydrogen bond via H(3B) to a N(2) atom. Overall, this results in the formation of a cesium-ammonia layer in the *ab*-plane shown in Figure 10. The cesium cations also form a network with the $B_{12}H_{12}^{2-}$ molecules in the *ab*-plane. Thus, the $B_{12}H_{12}^{2-}$ layers and the ammonia layers are connected by the Cs^+ cations as is shown in Figure 11. The *closo*-hydroborate cages form a face-centered packing which may be derived from the solvent free cubic structure of $Cs_2B_{12}H_{12}$.[27] Upon warming of **3** to room temperature

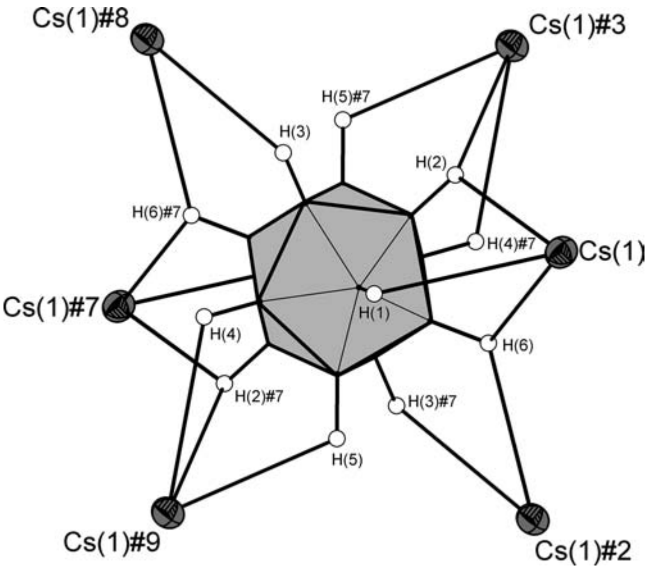

Figure 8. Coordination sphere of the $B_{12}H_{12}^{2-}$ cage. Its boron atoms are shown as a polyhedron. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Symmetry transformations to generate equivalent atoms: #2 $x + 1/2, -y + 1/2, -z$; #3 $x - 1/2, -y + 1/2, -z$; #7 $-x, -y, -z$; #8 $-x - 1/2, y - 1/2, z$; #9 $-x + 1/2, y - 1/2, z$.

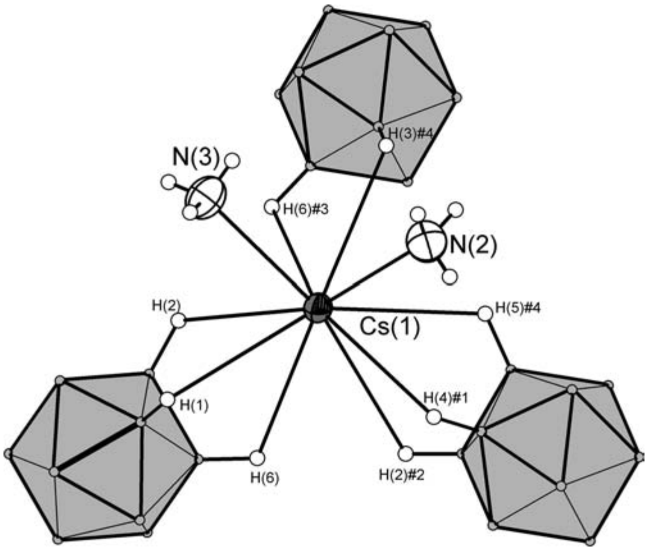

Figure 9. Coordination sphere of the cesium ion. Ellipsoids of the displacement parameters are drawn at 70% probability at 123 K. Boron atoms of the *closo*-hydroborate cage are shown as polyhedrons. Only H atoms coordinating to cesium are shown for clarity. Symmetry transformations to generate equivalent atoms: #1 $-x + 1/2, y + 1/2, z$; #2 $x + 1/2, -y + 1/2, -z$; #3 $x - 1/2, -y + 1/2, -z$; #4 $-x - 1/2, y + 1/2, z$.

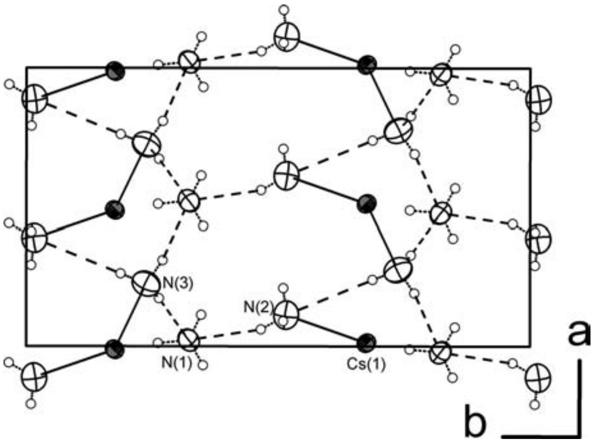

Figure 10. Cesium−ammonia network formed by N−H···N hydrogen bonds. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Symmetry transformations are omitted for clarity. Selected hydrogen bond lengths [Å] and angles [deg]: N(2)−H(2A) 0.86(3), N(1)···H(2A) 2.58, ∠N(2)−H(2A)···N(1) 153.4, N(3)−H(3A) 0.86(3), N(1)···H(3A) 2.48, ∠N(3)−H(3A)···N(1) 174.8, N(3)−H(3B) 0.82(3), N(2)···H(3B) 2.66, ∠N(3)−H(3B)···N(2) 171.7, N(3)−H(3C) 0.81(3), N(1)···H(3C) 2.59, ∠N(3)−H(3C)···N(1) 143.7.

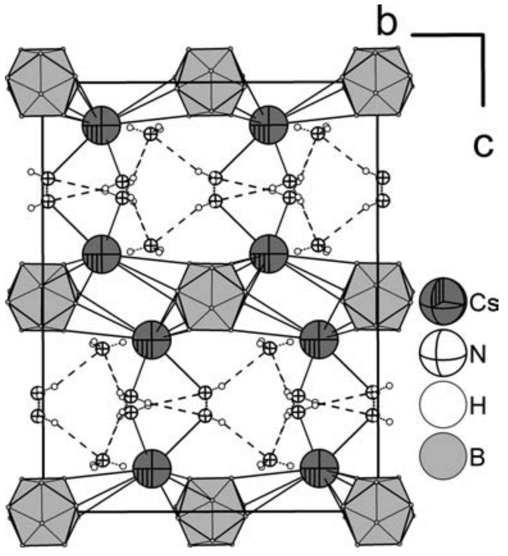

Figure 11. Connection of the ammonia and the $B_{12}H_{12}^{2-}$ layers via Cs^+ cations and the face centering of the cages. *closo*-Hydroborates are shown as polyhedrons with their H atoms omitted for clarity.

ammonia gas is liberated, and the resulting phase and its ammonia storage properties will be discussed elsewhere.

Dirubidium Decahydro-*closo*-borate Ammonia (1/5), $Rb_2B_{10}H_{10}\cdot 5NH_3$. Rb metal and $Li_2[B_{10}H_{10}]$ react in liquid ammonia solution according to eq 4:

$$2Rb + Li_2[B_{10}H_{10}] + 7NH_3 \rightarrow Rb_2[B_{10}H_{10}]\cdot 5NH_3 + H_2 + 2LiNH_2 \qquad (4)$$

Colorless crystals of **4** were obtained by decanting and analyzed by single crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pnma*. The decahydro-*closo*-decaborate cage is built up by seven boron and hydrogen atoms and their symmetry equivalents. All observed B−B distances to the apical boron atoms are found at 1.69 Å within standard deviation; the B−B bond lengths in the almost square antiprism are observed in the range between 1.81 and 1.84 Å. B−B−B angles are between 89.8(1)° and 90.2(1)° in the squares of the antiprism and between 57.2(1)° and 60.7(2)° of its triangles. Both apical boron atoms reside 1.09 Å above a rms plane through their corresponding boron squares, with the two planes being parallel within standard deviation. The boron−hydrogen bond lengths are approximately 1.1 Å. The $B_{10}H_{10}^{2-}$ cage is coordinated by six symmetry equivalent Rb^+ cations η^3- and η^2-like (see Figure 12) with Rb−H distances between 2.92 Å and 3.23 Å. The rubidium ion shows a coordination number of eleven, since one *closo*-hydroborate cage is coordinating η^3-like, two symmetry equivalent hydroborate ions are coordinating η^2-like and four symmetry independent ammonia molecules are connected (Figure 13). The ammonia molecules N(2) and N(3) are acting as bridging ligands between Rb(1) and its symmetry equivalent Rb(1)#4; N(4) bridges between Rb(1) and Rb(1)#5. Additionally N(2) forms two hydrogen bonds using H(2A) and H(2A)#4 to N(1) and N(1)#4, respectively (Figure 14). Thus, a $^{1}_{\infty}[Rb_2(NH_3)_5]$ chain is formed running along the *b*-axis where each rubidium ion is additionally surrounded by three $B_{10}H_{10}^{2-}$ cages. The unit cell of **4** is shown in Figure 15. Upon warming **4** to room temperature ammonia gas is liberated, and the resulting phase and its ammonia storage properties will be discussed elsewhere.

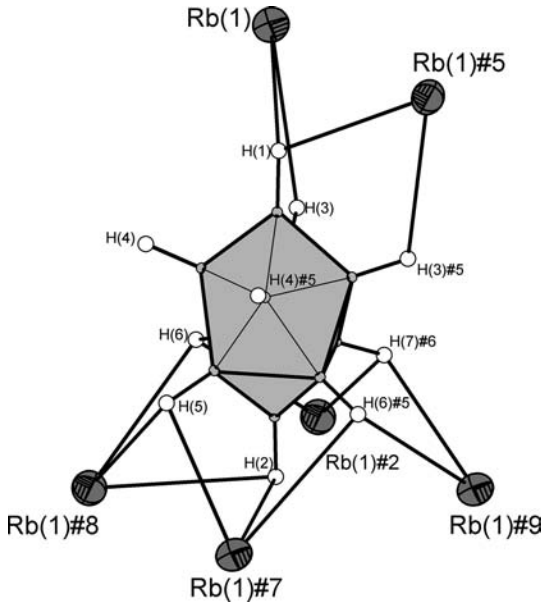

Figure 12. Coordination sphere of the $B_{10}H_{10}^{2-}$ anion. Boron atoms of the cage molecule shown as a polyhedron. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Selected bond lengths [Å]: Rb(1)−H(1) 3.01(2), Rb(1)−H(3) 3.21(2). Symmetry transformations to generate equivalent atoms: #2 $x + 1/2, y, -z + 3/2$; #5 $x, -y + 1/2, z$; #6 $x + 1, y, z$; #7 $-x + 1/2, y + 1/2, z + 1/2$; #8 $-x + 1/2, -y, z + 1/2$; #9 $x + 1/2, -y + 1/2, -z + 3/2$.

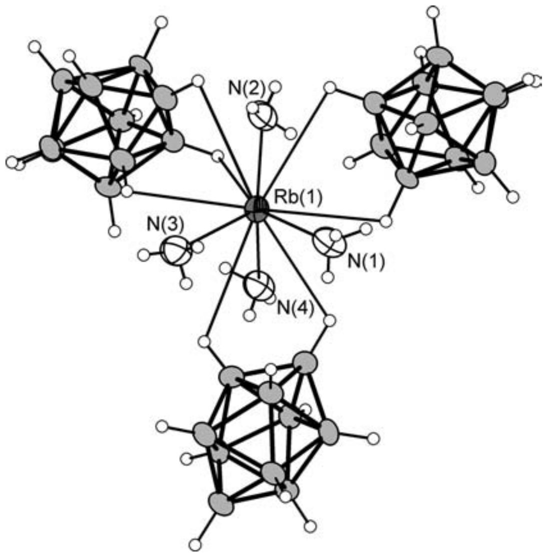

Figure 13. Coordination sphere of the rubidium cation. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Selected bond lengths [Å]: Rb(1)−N(1) 3.229(2), Rb(1)−N(2) 3.109(3), Rb(1)−N(3) 3.181(3), Rb(1)−N(4) 3.248(3).

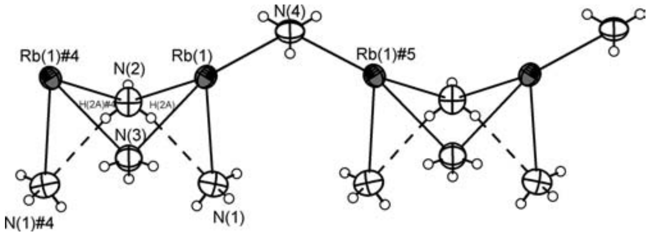

Figure 14. Projection of a fragment of the $^{1}_{\infty}[Rb_2(NH_3)_5]$ chain on the *bc*-plane. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K. Hydrogen bond lengths [Å] and angles [deg]: N(2)−H(2A) 0.76(5), N(1)···H(2A) 2.61, ∠N(2)−H(2A)···N(1) 142.3. Symmetry transformations to generate equivalent atoms: #4 $x, -y - 1/2, z$; #5 $x, -y + 1/2, z$.

■ CONCLUSION

A new synthetic route to several ammoniates of the alkali metal *closo*-hydroborates was developed. Such compounds are discussed in the literature as potential hydrogen storage materials. Four representatives were prepared, $[Li(NH_3)_4]_2B_{12}H_{12}\cdot 2NH_3$ (**1**), $Rb_2B_{12}H_{12}\cdot 8NH_3$ (**2**), $Cs_2B_{12}H_{12}\cdot 6NH_3$ (**3**) and $Rb_2B_{10}H_{10}\cdot 5NH_3$ (**4**), and structurally characterized by low-temperature X-ray diffraction in the solid state. We established substitution reactions, i.e., all of the dissolved alkali metals are able to replace tetrabutylammonium cations of a given *closo*-hydroborate forming a crystalline ammoniate of an alkali metal hydroborate. The second product, tetrabutylammonium amide, does not crystallize under the

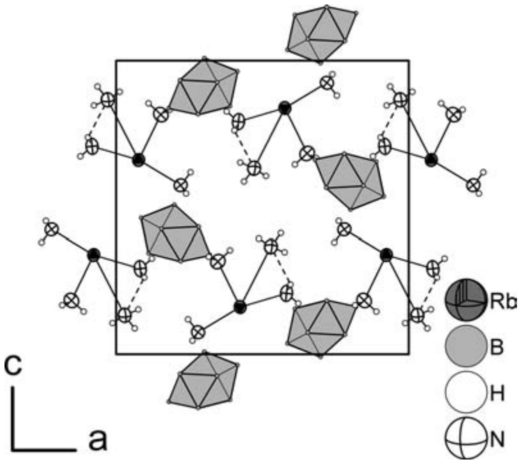

Figure 15. Projection on the *ac*-plane showing the packing of the $B_{10}H_{10}^{2-}$ cages around the $^{1}_{\infty}[Rb_2(NH_3)_5]$ strands. Boron atoms of the *closo*-hydroborate are shown as polyhedrons; hydrogens and coordinations to Rb^+ are omitted for clarity. Ellipsoids of the displacement parameters are drawn at the 70% probability level at 123 K.

conditions applied and was decanted. Also, the heavier congeners of the alkali metals are able to displace the lighter ones yielding the lighter alkali metal amides as byproducts. The amides were identified by single crystal and powder X-ray diffraction, as shown for compound **4** and earlier for cesium sodium *closo*-hydroborate.[8] As all of the cations in the presented structures, i.e., $[Li(NH_3)_4]^+$, Rb^+ and Cs^+, can be regarded as relatively soft acids according to the Pearson principle,[49] only minute symmetry deviations from I_h for the $B_{12}H_{12}^{2-}$ and from D_{4d} for the $B_{10}H_{10}^{2-}$ anions are observed.

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Notes

The authors declare no competing financial interest.

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