Journal of Solid State Chemistry 191 (2012) 279–282

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

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

Rapid Communication

Tetrabutylammonium cation in a homoleptic environment of borohydride ligands: $[(n\text{-Bu})_4N][BH_4]$ and $[(n\text{-Bu})_4N][Y(BH_4)_4]$

T. Jaroń [a],*, W. Wegner [a], M.K. Cyrański [a], Ł. Dobrzycki [a], W. Grochala [a,b],**

[a] Faculty of Chemistry, The University of Warsaw, Pasteura 1, 02093 Warsaw, Poland
[b] CENT, The University of Warsaw, Żwirki i Wigury 93, 02089 Warsaw, Poland

ARTICLE INFO

Article history:
Received 31 January 2012
Accepted 19 March 2012
This work is dedicated to Professor Tadeusz Marek Krygowski, at his 75th birthday
Available online 28 March 2012

Keywords:
Borohydrides
Homoleptic environment
Hydrogen storage
Thermal stability
Yttrium

ABSTRACT

A novel solvent-free dual-cation organic–inorganic derivative, tetrabutylammonium yttrium borohydride (TBAYB), has been prepared for the first time and structurally characterized together with its organic precursor, tetrabutylammonium borohydride (TBAB). Both compounds crystallize in monoclinic unit cells (TBAYB: $P2_1/c$, TBAB: $P2/c$) and they contain $[(n\text{-Bu})_4N]^+$ in a homoleptic environment consisting of BH_4^- ligands. Presence of large and lightweight Bu_4N^+ cations results in loose packing and low densities of both solids close to 1 g cm^{-3}. TBAB melts at *ca.* 130 °C and it decomposes thermally above 160 °C while TBAYB melts at temperature as low as 78 °C, and the melt is stable over an appreciable temperature range of *ca.* 150 °C. The low melting point of TBAYB is the second lowest among derivatives of yttrium rendering this compound a new ionic liquid above 78 °C.

1. Introduction

Hydrogen-rich borohydride (tetrahydridoborate) anion, BH_4^-, is contained in a large number of organic and inorganic compounds; search of CCSD and ICSD databases reveals over 8900 organic and *ca.* 100 inorganic structures containing this anion [1]. Borohydrides have traditionally been used as powerful reducing agents in organic synthesis [2]; recently they attract a lot of attention in terms of their hydrogen storage properties [3–6]. Structural characterisation is of value for understanding of the thermal decomposition process (hydrogen release) of such materials. It has been noticed that the temperature of hydrogen evolution [3,7] as well as the binding mode of $[BH_4]^-$ to the metal centre are correlated with electron acceptor properties of a metal, M, in quasi-binary metal borohydrides, $M(BH_4)_n$. Borohydrides of electropositive alkali metals (Li…Cs, Mg…Ba, etc.) are most thermally-stable and they exhibit predominantly ionic M…H–B interactions. Here, the tetrahedral $[BH_4]^-$ anions may act as mono-, bi- or tridentate ligands, thus coordinating metal cation via B–H corner, B–H_2 edge or B–H_3 face, respectively. In sharp contrast, borohydrides of more electronegative metals (for example Mn(II) [8], Zn(II) [9,10], Cu(I) [11], Al(III) [12], Y(III) [13], etc.) show enhanced covalence of the M…H bonds, which results in more directional bonding and lower temperatures of thermal decomposition. Covalence of M…H bonding influences the M–BH_4 coordination pattern, structural dimensionality and chemistry of these borohydrides [5,14]. For example, the extended 3D $[Y(BH_4)_{6/2}]$ framework of yttrium(III) borohydride with partly covalent metal–hydrogen bonding [13,15] is completely destroyed upon addition of one mol equivalent of alkali Lewis bases, and the 0D structure containing isolated $[Y(BH_4)_4]^-$ anions results. Simultaneously, the temperature of thermal decomposition markedly increases [16].

Here we extend our recent studies of lightweight H-rich yttrium-borohydride systems [15,16] and we describe a novel solvent-free dual-cation organic–inorganic derivative, i.e., tetrabutylammonium yttrium borohydride (TBAYB, Fig. 1); we also characterize its organic precursor, tetrabutylammonium borohydride (TBAB, Fig. 1). Both compounds contain $[(n\text{-Bu})_4N]^+$ in a homoleptic environment of BH_4^- ligands. We analyze changes of coordination of $[(n\text{-Bu})_4N]^+$ cation by borohydride ligands when a 'free' $[BH_4]^-$ anion is replaced by borohydride bound in a more complex $[Y(BH_4)_4]^-$ moiety. We also briefly discuss thermal properties of both compounds [17].

2. Experimental

2.1. Synthesis and preparation of single crystals

All reactions were performed and samples were stored in an inert gas (Ar) atmosphere of the MBRAUN Labmaster DP glovebox (< 1 ppm O_2, < 1 ppm H_2O). Toluene was dried over Na, $CHCl_3$ over

---

* Corresponding author.
** Corresponding author at: CENT, The University of Warsaw, Żwirki i Wigury 93, 02089 Warsaw, Poland.

E-mail addresses: tjaron@chem.uw.edu.pl (T. Jaroń), wg22@cornell.edu (W. Grochala).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.03.040

P_4O_{10}. Commercially available tetrabutylammonium borohydride (Aldrich) has been used for powder X-ray diffraction (PXD) measurements. Crystallisation of TBAB was carried out by dissolving 220 mg of TBAB powder in a mixture of 7 ml toluene and *ca.* 0.25 ml chloroform and slow evaporation. TBAYB has been synthesised by milling of TBAB with $Y(BH_4)_3$ in 1: 1 M ratio in a stainless steel bowl using a Testchem vibrational mill. The milling was done in 5 min periods; the milling bowl was cooled periodically with liquid N_2 to avoid thermal decomposition of the product. $Y(BH_4)_3$ precursor has been used as prepared in a mechanochemical synthesis from YCl_3 to 3 $LiBH_4$ and it contained *ca.* 50 wt% LiCl [15]. TBAYB was crystallised from chloroform; 300 mg of the mixture of TBAYB and LiCl in a *ca.* 1: 3 M ratio was dispersed in 10 ml chloroform, LiCl residue was separated by filtration, and the solution was left for crystallization.

2.2. Powder X-ray diffraction (PXD)

Solid products (sealed with wax inside the 0.5 mm quartz capillaries) were investigated by X-ray powder diffraction using Panalytical X'Pert Pro diffractometer (Co$K_{\alpha1}$ and Co$K_{\alpha2}$ intensity ratio of *ca.* 2:1). Pattern indexing was performed in X-Cell [18], structure solution in FOX [19] and Rietveld refinement in Jana2006 [20]. A two-phase refinement was used for TBAYB mixed with LiCl by-product. The measured and calculated powder X-ray diffraction profiles and a difference curves as well as the positions of calculated reflexes, have been showed in Supplementary Information.

2.3. Single crystal diffraction

The single crystal measurements for TBAYB were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated MoK_α radiation. The crystal was positioned at 62 mm from the CCD camera. 318 frames were measured at 0.75° intervals with a counting time of 80 s. The data were corrected for Lorentz and polarization effects. Analytical correction for absorption was applied [21]. Data reduction and analysis were carried out with the Oxford Diffraction programs [22]. The structure was solved by direct methods [23] and refined using SHELXL [24]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. [25]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms, except at boron were placed in calculated positions and refined within riding model. Their isotropic ADPs were set to be 1.2 or 1.5 times bigger than U_{eq} of corresponding heavy atoms. The other hydrogen atoms were located from a difference maps and their positions refined isotropically.

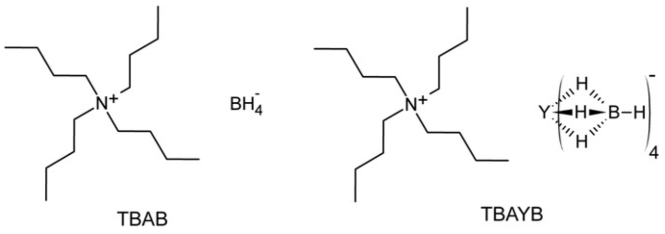

Fig. 1. Structural formulae of tetrabutylammonium borohydride (TBAB, left) and tetrabutylammonium yttrium borohydride (TBAYB, right).

The measurements for TBAB were also performed but due to twinning and substantial disorder in the structure the refinement is of poorer quality. Further details of the crystal structures may be obtained from Cambridge Crystallographic Data Centre, on quoting the CCD numbers 863958 (TBAYB, RT) and 863590 (TBAYB, 100 K). The crystal data for TBAB (both 100 K and RT, see comment above) are contained in the ESI.

2.4. Thermogravimetry/differential scanning calorimetry/evolved gas analysis studies

The details of our experimental TGA/DSC/EGA setup have been described elsewhere [15,16].

3. Results and discussion

TBAB has been first mentioned in 1971, but the crystal structure of this compound has not been reported so far [26]. On the other hand, TBAYB is a new compound, homologous to the recently synthesized tetramethylammonium salt [16]. However, in sharp contrast to tetramethylammonium derivative, TBAYB is soluble in organic solvents (for example chloroform) which facilitates its purification, removal of a dead mass of lithium chloride (coming from synthesis of $Y(BH_4)_3$ precursor) and subsequent crystallisation.

TBAYB has been synthesised in a virtually quantitative mechanochemical reaction (1) from TBAB to $Y(BH_4)_3$ containing LiCl:

$$Y(BH_4)_3+3\ LiCl+[(n\text{-}C_4H_9)_4N][BH_4]\rightarrow[(n\text{-}C_4H_9)_4N][Y(BH_4)_4]+3\ LiCl \quad (1)$$

High yield of reaction (1) has been confirmed by PXD phase analysis (the calculated TBAYB content of 75.8 wt% is identical within error limit to the value of 75.4 wt% corresponding to 100% yield). The structural results for TBAB and TBAYB from room-temperature powder diffraction and single crystal 100 K studies are presented in Table 1. Selected bond lengths and other geometric parameters are given in Table 2. Both compounds adopt monoclinic

Table 1
Comparison of unit cell parameters for TBAB and TBAYB at 100 K and 298 K.

Compound	TBAB		TBAYB*	
T (K)	100 (monocrystal)	298 (powder)	100 (monocrystal)	298 (powder)
Space group	$P2/c$	$P2/c$	$P2_1/c$	$P2_1/c$
a (Å)	26.003(3)	25.9747(7)	11.0453(5)	11.4181(10)
b (Å)	13.0324(9)	13.5175(3)	20.0099(9)	20.510(3)
c (Å)	25.392(3)	26.1404(6)	14.7204(8)	15.2811(19)
β (°)	118.583(13)	118.7281(9)	127.980(5)	129.464(8)
V (Å^3)	7556.16	8048.5	2564.44	2762.77
Z	16	16	4	4
d (g cm^{-3}) calc.	0.905	0.847	1.012	0.939

* This monoclinic unit cell may be transformed to a quasi-orthorhombic unit cell ($a^*=17.6567$ Å, $b^*=20.5222$ Å, $c^*=15.2912$ Å, $\beta^*=87.514°$) via matrix (201,010,001).

Table 2
Comparison of geometries of $[(n\text{-Bu})_4N]^+$ cation in several structurally characterized derivatives. Selected distances are given in (Å) and bond angles in (°). Cat.–an. — distance between cation and central atom of anion. Type of coordination of $[(n\text{-Bu})_4N]^+$ by anions is described. *T*—temperature, *RT*—room temperature, *CN*—coordination number.

Anion	**BH_4^-**	**$[Y(BH_4)_4]^-$**	**I^-**	**PF_6^-**	**HSO_4^-**	**$FeCl_4^-$**	**$[(n\text{-Bu})_4B]^-$**
T (K)	RT	100	100	110	120	RT	RT
Space group	*P*2/*c*	*P*2$_1$/*c*	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*	*Pnna*	*I*4$_1$/*a*
Ref.	This work	This work	[31]	[32]	[33]	[34]	[28]
Bond lengths							
C–N min.	1.483(14)	1.516(3)	1.517(2)	1.515(2)	1.505(5)	1.507(3)	1.519(3)
C–N max.	1.546(12)	1.529(3)	1.522(2)	1.529(2)	1.532(5)	1.524(3)	1.519(3)
C–C min.	1.46(3)	1.516(2)	1.516(2)	1.516(3)	1.349(8)	1.440(6)	1.456(7)
C–C max.	1.551(13)	1.533(3)	1.525(3)	1.531(2)	1.657(9)	1.523(5)	1.511(4)
Bond angles							
C–N–C min.	91.8(9)	108.5(2)	108.6(1)	108.4(1)	105.0(3)	108.5(2)	105.0(1)
C–N–C max.	119.2(13)	111.1(2)	111.1(1)	111.2(1)	112.2(3)	111.6(2)	111.8(1)
N–C–C min.	111.7(7)	115.4(2)	114.9(1)	114.6(1)	114.5(3)	117.1(2)	115.9(2)
N–C–C max.	117.2(10)	116.4(2)	115.4(1)	116.8(1)	117.2(3)	117.7(2)	115.9(2)
C–C–C min.	102.1(11)	108.6(2)	109.8(1)	109.6(1)	103.8(4)	109.7(3)	112.8(3)
C–C–C max.	121.4(12)	113.4(2)	111.3(2)	114.4(1)	135.7(6)	116.2(3)	117.8(4)
Cation–anion packing							
Cat.–an. min.	4.404(18)	5.735(2)	5.048(1)	5.111(1)	4.596(3)	5.7858(4)	5.2901(1)
Cat.–an. coordination	Trigonal+tetrahedral	Tetrahedral	Square	Trigonal pyramid	Trigonal+tetrahedral	Trigonal bipyramid	Linear
Cat.–an. CN [30]	3, 4	4	4	4	4	5	2

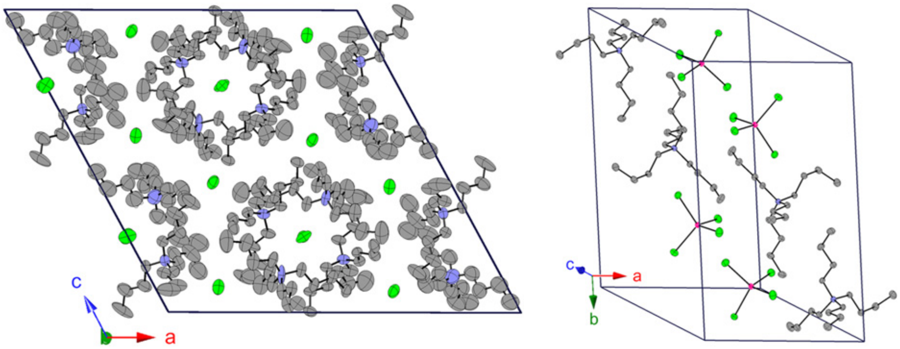

Fig. 2. The unit cell of tetrabutylammonium borohydride (TBAB), left, and tetrabutylammonium yttrium borohydride (TBAYB), right. The atoms are represented by 50% probability displacement ellipsoids. Hydrogen atoms have been removed for clarity. C—grey, N—blue, B—green, Y—red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

unit cells, Fig. 2, with TBAYB taking a centrosymmetric *P*2$_1$/*c* while TBAB a related non-centrosymmetric *P*2/*c* space group. Presence of large and lightweight Bu_4N^+ cations results in loose packing and low densities of both solids (close to 1 g cm^{-3}, comparable with the those for similar tetraalkylammonium salts, e.g., $[(CH_3)_4N][BH_4]$ 0.834 [27], $[(CH_3)_4N][Y(BH_4)_4]$ 0.955 [28], $[(n\text{-Bu})_4N][(n\text{-Bu})_4B]$ 0.846 [28]; $[(n\text{-}C_3H_7)_4N][BF_4]$ 1.141 [29], all in [g cm^{-3}]).

The geometry of $[(n\text{-Bu})_4N]^+$ cation in TBAB is considerably deformed from the one based on quasi-tetrahedral model, Table 2. The longest and shortest C–C(N) bond lengths differ by 0.09 Å, while selected bond angles depart from 109.47° by up to 12°; this is reminiscent of the degree of deformation of $[(n\text{-Bu})_4N]^+$ cation observed for derivatives containing small HSO_4^- and $FeCl_4^-$ anions. However, the $[(n\text{-Bu})_4N]^+$ cations of TBAYB are less strained, with the differences in extreme values of C–C(N) bonds and C–C–C(N) angles not exceeding 0.02 Å, and 5°, respectively. Similar weakly strained cations are seen for $[(n\text{-Bu})_4N]^+$ derivatives with larger or weakly coordinating anions such as $[(n\text{-Bu})_4B]^-$ and PF_6^- (Table 2).

As far as the angles between the skeletal atoms are concerned, the N–C–C angles are the most obtuse in both tetrabutylammonium compounds studied. This feature may be explained by the steric interactions between the hydrogen atoms of the neighbouring *n*-Bu chains as well as by directional interaction of positively charged N centre of $[(n\text{-Bu})_4N]^+$ cations with neighbouring anions.

There are four independent $[(n\text{-Bu})_4N]^+$ cations and six independent BH_4^- anions in the unit cell of TBAB. The packing pattern in TBAB – as seen from N–B sublattice – is a 3-D network of interesting topology and approximately *C*2/*c* symmetry (Fig. 3). Distorted trigonal and distorted tetrahedral coordinations are observed for different types of N and B atoms of the N–B sublattice. Such packing pattern has not been observed so far for any other $[(n\text{-Bu})_4N]^+$ derivative. The N–B distances range from 4.404(18) Å to 4.964(9) Å and they are similar to those found for tetramethylammonium borohydride (4.533(6) Å × 4 and 5.246(8) Å × 4) [27,35].

The crystal structure of TBAYB is simpler than that of TBAB. There is only one independent $[(n\text{-}C_4H_9)_4N]^+$ cation and one independent $[Y(BH_4)_4]^-$ anion in the unit cell of TBAYB (Fig. 4). The cation is surrounded by four anions at separation ranging from 5.735(2) to 6.655(1) Å (as measured by N–Y distances), forming a distorted NY_4 tetrahedron. The four closest N–Y distances in TBAYB are comparable with six such distances in homologous $[(CH_3)_4N][Y(BH_4)_4]$, 5.804(7)–6.037(8) Å [16]. The shortest N–B separations (Table 2) are close to those seen for TBAB and $[(CH_3)_4N][Y(BH_4)_4]$ [16,35]. The coordination of Y atoms by N centres can be described as a deformed trigonal pyramid, with three closest N atoms nearly coplanar with yttrium (within *ca.* 5°). A different pattern is observed in another organic derivative containing $[Y(BH_4)_4]^-$ ions, $[(CH_3)_4N][Y(BH_4)_4]$, where much smaller

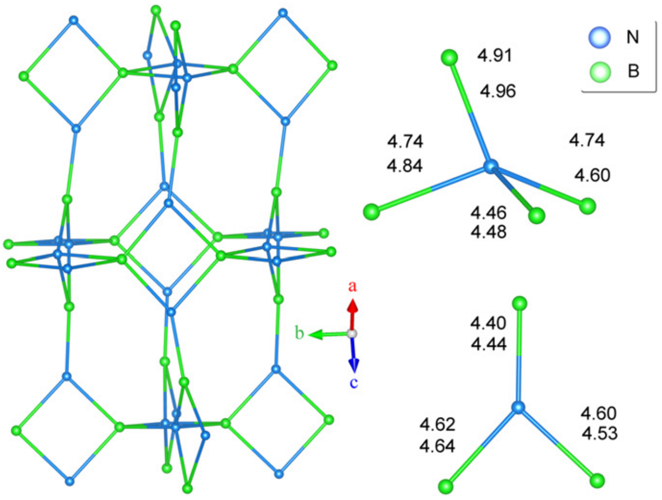

Fig. 3. The packing pattern in TBAB as represented by the N–B sublattice (C and H atoms have been removed for clarity). The interatomic separations are given in [Å] for the first (upper) and the second (lower) of trigonal and tetrahedral nitrogen atoms (rounded to 0.0 Å). N and B atoms are stick-bonded for clarity.

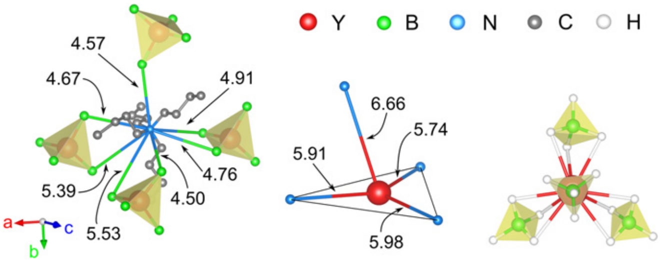

Fig. 4. A closer view of selected structural components of TBAYB: coordination of n-Bu$_4$N by YB$_4$ tetrahedra (left); coordination of Y by n-Bu$_4$N, represented by nitrogen atoms (centre); $[Y(BH_4)_4]^-$ group (right). The interatomic distances are given in [Å] (rounded to 0.01 Å).

tetramethylammonium cations form a deformed octahedron around yttrium centre at separation of 5.804(6)–6.037(8) Å [16].

TBAYB is, after K^+ and Me_4N^+ derivatives [16], the third known compound containing $[Y(BH_4)_4]^-$ anions with the tetrahedral YB$_4$ skeleton. The YB$_4$ tetrahedra are quite regular, with almost equal four Y–B bonds (the bond length differences are <0.01 Å) and the B–Y–B angles close to tetrahedral ($\pm 2^\circ$). As in all known $[Y(BH_4)_4]^-$ [16] and $[Sc(BH_4)_4]^-$ [5,36–38] compounds, the $[BH_4]^-$ groups serve as tridentate ligand to metal centre in TBAYB, with short Y–H distances of 2.20(3)–2.33(2) Å.

The combined DSC/TGA/EGA study shows that TBAB melts at *ca.* 130 °C and it decomposes above 160 °C (see Supplementary Information). On the other hand, TBAYB decomposes endothermally above 230 °C, thus at temperature similar to that for tetramethylammonium derivative [16]. Interestingly, thermal decomposition of TBAYB is preceded by melting at *ca.* 78 °C, the melt being stable over an appreciable temperature range of 150 °C. The low melting point renders TBAYB ionic liquid above 78 °C and also the second lowest-melting derivative of yttrium, with tris(butylcyclopentadienyl) yttrium(III) (which is liquid at room temperature) holding the record-low value of a freezing point.

Acknowledgments

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw. TJ appreciates the financial support from the Faculty of Chemistry, University of Warsaw for (BST 120000-501/86-DSM100100).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.03.040.

References

[1] 8907 and 98, respectively [accessed 19.12.2011].
[2] M.V.N. de Souza, T.R.A. Vasconcelos, Appl. Organomet. Chem. 20 (2006) 798.
[3] W. Grochala, P.P. Edwards, Chem. Rev. 104 (2004) 1283.
[4] A.J. Churchard, et al., Phys. Chem. Chem. Phys. 13 (2011) 16955.
[5] L.H. Rude, T.K. Nielsen, D.B. Ravnsbæk, U. Bösenberg, M.B. Ley, B. Richter, L.M. Arnbjerg, M. Dornheim, Y. Filinchuk, F. Besenbacher, T.R. Jensen, Phys. Status Solidi A 208 (2011) 1754. and the references therein.
[6] H.-W. Li, Y. Yan, S.-I. Orimo, A. Züttel, C.M. Jensen, Energies 4 (2011) 185.
[7] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, S.I. Orimo, Phys. Rev. B 74 (2006) 45126.
[8] R. Černý, N. Penin, H. Hagemann, Y. Filinchuk, J. Phys. Chem. C 113 (2009) 9003.
[9] E. Wiberg, W. Henle, Z. Naturforsch. 7b (1952) 579.
[10] E. Jeon, Y.W. Cho, J. Alloys Compd. 422 (2006) 273.
[11] E. Wiberg, W. Henle, Z. Naturforsch. 7b (1952) 582.
[12] H.I. Schlesinger, R.T. Sanderson, A.B. Burg, J. Am. Chem. Soc. 62 (1940) 3421.
[13] T. Sato, K. Miwa, Y. Nakamori, K. Ohoyama, H. Li, T. Noritake, M. Aoki, S. Towata, S. Orimo, Phys. Rev. B 77 (2008) 104114.
[14] D.B. Ravnsbæk, Y. Filinchuk, R. Černý, T.R. Jensen, Z. Kristallogr. 225 (2010) 557.
[15] T. Jaroń, W. Grochala, Dalton Trans. 39 (2010) 160.
[16] T. Jaroń, W. Grochala, Dalton Trans. 40 (2011) 12808.
[17] E.A. Nickels, M.O. Jones, W.I.F. David, S.R. Johnson, R.L. Lowton, M. Sommariva, P.P. Edwards, Angew. Chem. Int. Ed. 47 (2008) 2817.
[18] M. Neumann, J. Appl. Crystallogr. 36 (2003) 356.
[19] V. Favre-Nicolin and R. Černý, J. Appl. Crystallogr., 2002, 35, 734. See also: Fox, Free Objects for Crystallography, 〈http://objcryst.sourceforge.net〉.
[20] V. Petricek, M. Dusek, L. Palatinus, Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic (Jana 2006).
[21] R.E.D. CrysAlis, Oxford Diffraction Ltd.,Version 1.171.28. Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R. C. Clark & J. S. Reid.
[22] C.C.D. CrysAlis, Oxford Diffraction Ltd., Version 1.171.28; CrysAlis RED, Oxford Diffraction Ltd.,Version 1.171.28.
[23] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[24] G.M. Sheldrick, SHELXL93. Program for the Refinement of Crystal Structures., Univ. of Göttingen, Germany.
[25] A. J. C. Wilson (Ed.), International Tables for Crystallography, Kluwer: Dordrecht, 1992, Vol. C.
[26] L.V. Titov, L.A. Gavrilova, E.R. Eremin, S.S. Mishchenchuk, V.Ya. Rosolovskii, Russ. Chem. Bull. 20 (1971) 1266.
[27] T. Jaroń, W. Grochala, Acta Crystallogr., Sect. E 67 (2011) o2171.
[28] B. Kaitner, V. Stilinović, Acta Crystallogr., Sect. A 66 (2010) 441.
[29] G. Giuseppetti, F. Mazzi, C. Tadini, P. Ferloni, G. Zabinska, S. Torre, Z. Kristallogr. 212 (1997) 367.
[30] The coordination numbers in these compounds are well-defined. The difference in maximum and minimum distances between the cation and anion central atoms are below 1 Å for anions within the coordination sphere of a cation. The second coordination sphere is separated by >1.5 Å from the first one.
[31] W. Prukała, B. Marciniec, M. Kubicki, Acta Crystallogr., Sect. E 63 (2007) o1464.
[32] Z. Stein, I. Goldberg, Acta Crystallogr., Sect. E 61 (2005) o272.
[33] M.E. Light, P.A. Gale, M.B. Hursthouse, Acta Crystallogr., Sect. E 57 (2001) o705.
[34] M.T. Hay, S.J. Geib, Acta Crystallogr., Sect. E 61 (2005) m190.
[35] Both TBAB and TBAYB form predominantly ionic networks, where packing of counterions depends mostly on steric factors. However, the flexibility of the N–C–C skeleton enables $[BH_4]^-$ or $[Y(BH_4)_4]^-$ anions to closely approach the positively charged nitrogen centre. Therefore the shortest cation–anion separations in TBAB and TBAYB are similar to those seen for tetramethylammonium homologues with much smaller cations.
[36] H. Hagemann, M. Longhini, J.W. Kaminski, T.A. Wesolowski, R. Černý, N. Penin, M.H. Sørby, B.C. Hauback, G. Severa, C.M. Jensen, J. Phys. Chem. A 112 (2008) 7551.
[37] R. Černý, G. Severa, D.B. Ravnsbæk, Y. Filinchuk, V.D. Anna, H. Hagemann, D. Haase, C.M. Jensen, T.R. Jensen, J. Phys. Chem. C 114 (2010) 1357.
[38] R. Černý, D.B. Ravnsbæk, G. Severa, Y. Filinchuk, V.D. Anna, H. Hagemann, D. Haase, J. Skibsted, C.M. Jensen, T.R. Jensen, J. Phys. Chem. C 114 (2010) 19540.