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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*

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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

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[*] 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).

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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 ($CoK_{\alpha 1}$ and $CoK_{\alpha 2}$ 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.

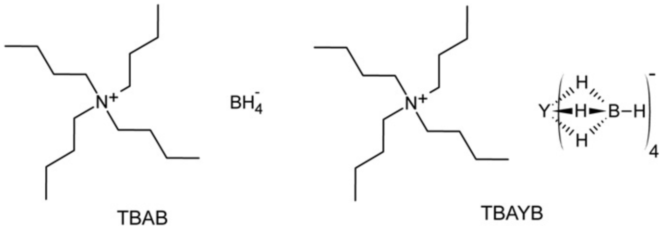

Fig. 1. Structural formulae of tetrabutylammonium borohydride (TBAB, left) and tetrabutylammonium yttrium borohydride (TBAYB, right).

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, β^*=87.514°) via matrix (201,010,001).