Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 13119

Received 30th April 2015,
Accepted 4th June 2015

DOI: 10.1039/c5dt01633a

www.rsc.org/dalton

Alkoxy substituted halogenated *closo*-dodecaborates as anions for ionic liquids†

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Halogenated and alkoxylated *closo*-dodecaborates $[B_{12}X_{11}OR]^{2-}$ (X = Cl, Br; R = propyl, octyl, dodecyl) have been synthesized by halogenation of the known $[B_{12}H_{11}OH]^{2-}$ anion followed by alkylation in the superbasic medium DMSO/KOH. The obtained sodium salts were transformed by simple metathesis reactions in aqueous solution to the tetrabutylammonium ($[NBu_4]^+$) and 1-hexyl-3-methylimidazolium ($[C_6mim]^+$) salts. All compounds were fully characterized by heteronuclear NMR, IR and Raman spectroscopy, ESI mass spectrometry, and thermal analytical measurements. Selected anions were also structurally characterized as their $[Ph_4P]^+$ salts by single crystal X-ray diffraction. The $[C_6mim]^+$ salts are thermally stable up to more than 300 °C and show clear melting points. Surprisingly, the compound $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ having the short propyl group bound to the boron cluster shows the lowest melting point (96 °C) of all the investigated compounds. Thus this compound is a rare member of the class of ionic liquids consisting of dianions.

Introduction

Halogenated boron cluster anions exhibit exceptional chemical and thermal stability. For instance the chlorinated *closo*-dodecaborate $[B_{12}Cl_{12}]^{2-}$ and 1-carba-*closo*-dodecaborate $[HCB_{11}Cl_{11}]^-$ anions have decomposition temperatures higher than 600 °C and 400 °C,[1] respectively, and have been widely applied as weakly coordinating anions, for instance to stabilize reactive cations.[2] These properties make these boron cluster anions potentially interesting for applications in thermally stable ionic liquids.[3] Despite the still increasing importance of ionic liquids,[4] the number of boron cluster-based ionic liquids is still limited. Salts containing carborates[5] and stannaborates[6] show quite low melting points. In contrast, the melting points of salts based on the dianionic perchlorinated dodecaborate $[B_{12}Cl_{12}]^{2-}$,[5e,7] which has been introduced by us as a weakly coordinating anion,[8] are higher. Table 1 summarizes the melting points of selected low melting salts containing boron cluster anions.

Table 1 Melting points of selected low melting salts containing boron cluster anions

Compound	T_m/°C	Ref.
$[C_2mim]_2[B_{12}Cl_{12}]$	265	5*e*
$[C_{16}mim]_2[B_{12}Cl_{12}]$	105	5*e*
$[N_{2\,2\,2\,4}]_2[B_{12}Cl_{12}]$	>300	7
$[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]$	104	7
$[C_2mim][SnB_{11}H_{11}Et]$	106	6
$[C_4mim][SnB_{11}H_{11}Bu]$	55	6
$[C_2mim][HCB_{11}H_{11}]$	122	5*a*
$[C_2mim][n\text{-propyl-}CB_{11}H_{11}]$	45	5*a*
$[C_4mim][Et_3NB_{12}H_{11}]$	128–130	10*c*
$[C_4mim][dodecyl_3NB_{12}H_{11}]$	25	10*c*

The very high price of the 1-carba-*closo*-dodecaborates prevents their broad application, while the parent *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ and its derivatives are relatively cheap and easily available.[9] Therefore attempts have been made to develop ionic liquids based on trialkylammonio substituted single charged *closo*-dodecaborate anions $[R_3NB_{12}H_{11}]^-$.[10] These anions led to salts of satisfying low melting points, but the chemical stability of these compounds is still in need of improvement, due to the presence of potentially reactive boron–hydrogen bonds. Very recently, we reported the chlorinated derivative $[B_{12}Cl_{11}NMe_3]^-$,[11] which possesses improved chemical, thermal, and electrochemical stability. However, all attempts to introduce longer alkyl chains on the nitrogen atom have not been successful so far. To take advantage of the cheap price or simple synthesis, respectively, of the parent *closo*-dodecaborate cluster and the superior chemical and thermal properties of the perhalogenated derivatives we attempted to prepare low melting salts of the hitherto unknown halogenated $[B_{12}X_{11}OR]^{2-}$ anion (X = Cl, Br, R =

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† Electronic supplementary information (ESI) available. CCDC 1057639–1057644. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01633a

alkyl). Herein the synthesis, full spectroscopic characterization, thermal and electrochemical properties, and crystal structures are reported.

Results and discussion

Synthesis of the halogenated and alkoxylated clusters $[B_{12}X_{11}OR]^{2-}$ (X = Cl, Br, R = alkyl)

We started from the known hydroxylated cluster $[B_{12}H_{11}OH]^{2-}$, which was obtained by a literature procedure.[12] Halogenation and *O*-alkylation gives the halogenated and alkoxylated clusters $[B_{12}X_{11}OR]^{2-}$. In principle, these two steps can be performed in two different chronological orders. However, from the synthesis of $[B_{12}Cl_{11}NMe_3]^{-}$ it is known that halogenation of an already *N*-alkylated cluster leads to two problems.[11] The halogenation is sterically hindered and thus yields incompletely halogenated products and secondly the already present organic group may be partly halogenated as well. Therefore, we preferred to perform the halogenation first followed by a subsequent *O*-alkylation. The halogenation reactions were carried out in a boiling aqueous (for $[B_{12}Cl_{11}OH]^{2-}$) or aqueous/methanolic (for $[B_{12}Br_{11}OH]^{2-}$) solution and by using the elemental halides as halogenation reagents.[1c,9] Due to the presence of small amounts of unreacted $[B_{12}H_{12}]^{2-}$ and dihydroxylated $[B_{12}H_{10}]^{2-}$, small amounts of $[B_{12}X_{12}]^{2-}$ (X = Cl, Br) and $[B_{12}X_{10}(OH)_2]^{2-}$ (X = Cl, Br) were obtained as impurities. The boron–oxygen bond is stable under these reaction conditions, thus only the hydrogen atoms are replaced by halides as required. The subsequent alkylation was performed in the superbasic medium KOH and DMSO.[13] Scheme 1 summarizes the complete reaction pathway.

Spectroscopic characterization of $[B_{12}X_{11}OH]^{2-}$ and $[B_{12}X_{11}OR]^{2-}$ (X = Cl, Br; R = alkyl)

All new compounds were fully characterized by heteronuclear NMR spectroscopy and by vibrational spectroscopy. The full set of data and all actual spectra are included in the ESI (section S.2†). The ^{11}B NMR spectra of the hydroxylated cluster $[B_{12}H_{11}OH]^{2-}$ strongly depend on the solvent. In organic solvents and water (pH 7) the spectrum shows a 1 : 5 : 5 : 1 pattern. The oxygen-bonded boron atom B1 is observed at about 5 ppm, the five membered rings between −15 and −18 ppm and the antipodal boron atom B12 at −24 ppm. In strongly acidic solution the ^{11}B NMR signal of the boron atom B1 is shifted to a higher field by about 5 ppm, while the chemical shifts of the other boron atoms are not affected. This is in agreement with protonation of the hydroxyl group in acidic solutions. After halogenation the spectrum changes from a 1 : 5 : 5 : 1 to a 1 : 10 : 1 pattern (chlorination or bromination does not lead to a difference), because the signals of the B2–6 and B7–11 atoms overlap. The boron atom B1 is significantly shifted to a higher field, while the antipodal boron atom B12 is shifted to a lower field. Subsequent alkylation does not change the ^{11}B NMR pattern. Table 2 summarizes the ^{11}B NMR chemical shift of the boron clusters.

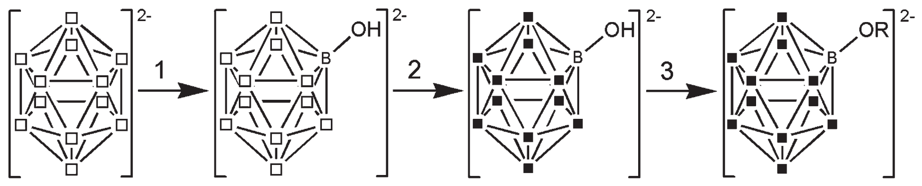
The IR spectra of salts of the $[B_{12}X_{11}OH]^{2-}$ (X = H, Cl, Br) anions show the O–H vibration at about 3600 cm^{-1} (Fig. S16 and S19), which disappears after *O*-alkylation. In the alkoxy substituted derivatives the characteristic C–H vibration is present, whose intensity increases with the length of the alkyl chain. All IR- and Raman spectra are depicted in the ESI.† Negative ESI-mass spectra of all the compounds show the complete anions as the main signal. The isotopic patterns are in good compliance with the expected and simulated spectra. In addition, ion pairs were also detected in agreement with our previous reports.[14]

Thermal analysis

The thermal properties of the tetrabutylammonium and the 1-hexyl-3-methylimidazolium ($[C_6mim]^+$) salts of the new $[B_{12}X_{11}OR]^{2-}$ anions were investigated (see section S.2.10 in the ESI† for details). Thermogravimetric analyses (TGA) were carried out to investigate the decomposition reactions of the salts, and differential scanning calorimetry (DSC) measurements gave the melting points. The tetrabutylammonium salts have significantly lower decomposition temperatures than the $[C_6mim]^+$ salts and do not melt below 300 °C, therefore the

Table 2 ^{11}B NMR shifts [ppm] of selected boron clusters in different solvents

	B1	B2–B7	B8–B11	B12
$B_{12}H_{11}OH$ (D_2O, pH 7)	5.4	−15.5	−18.0	−24.1
$B_{12}H_{11}OH$ (D_2O, pH 1)	0.7	−17.8	−19.1	−23.7
$B_{12}H_{11}OH$ (CD_3CN)	5.5	−15.7	−17.9	−24.0
$B_{12}Cl_{11}OH$	−7.3	−13.8	−13.8	−15.5
$B_{12}Cl_{11}O$-R	−7.5	−13.8	−13.8	−15.6
$B_{12}Br_{11}OH$	−4.2	−14.1	−14.1	−16.6
$B_{12}Br_{11}O$-R	−4.4	−14.4	−14.4	−16.7



Scheme 1 Reaction pathway to $[B_{12}X_{11}OR]^{2-}$ (X = Cl, Br, R = alkyl). 1. H_2SO_4/H_2O, ΔT; 2. Cl_2 in H_2O or Br_2 in H_2O/methanol, ΔT; 3. R–Br in KOH/DMSO, r.t. (□ = B–H, ■ = B–Cl/Br; R = alkyl).

Table 3 Compilation of the thermo-analytical data for $[C_6mim]_2[B_{12}X_{11}OR]$ (X = Cl, Br; R = propyl, octyl, dodecyl)

Anion	M_p [a]/°C	Experimental mass loss[b]/%	Theoretical mass loss[c]/%	T_d [d]/°C
$[B_{12}Cl_{11}O\text{-propyl}]^{2-}$	94–98 (96)	5.15	4.72	350
$[B_{12}Cl_{11}O\text{-octyl}]^{2-}$	138–143 (145)	12.97	11.51	368
$[B_{12}Cl_{11}O\text{-dodecyl}]^{2-}$	136–142 (144)	16.08	16.29	355
$[B_{12}Br_{11}O\text{-propyl}]^{2-}$	158–160 (161)	3.95	3.07	335
$[B_{12}Br_{11}O\text{-octyl}]^{2-}$	120–124 (126)	8.89	7.69	349
$[B_{12}Br_{11}O\text{-dodecyl}]^{2-}$	128–134 (139)	7.46	11.08	240

[a] The melting points were measured using Stuart SMP10 melting point apparatus. Values in brackets were obtained by differential scanning calorimetry. [b] Mass loss for the first decomposition step based on the TGA measurements. [c] Calculated for the loss of the alkyl chain of the anion. [d] Decomposition temperature

following discussion is restricted to the $[C_6mim]^+$ salts. All thermo-analytical data referring to the $[C_6mim]^+$ salts are summarized in Table 3.

The DSC measurements show only one endothermic peak in the heating curve and one exothermic peak in the cooling curve for most compounds. The melting points are in very good agreement with the melting points obtained by classical optical melting point determination. Also the heating and cooling curves obtained by DSC for $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]^{2-}$ are depicted in Fig. 1. There is no clear dependency of the melting points on either the length of the alkyl chain or the halogen atoms on the cluster. The salt $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ shows the lowest melting point (96 °C) of all the investigated compounds and can be classified as an ionic liquid. Surprisingly, the smaller chloro substituted anion with the shortest alkyl chain leads to the lowest melting point among all the anions in this study. A similar behavior has also been observed for the carborane ionic liquids $[C_2mim][RCB_{11}H_{11}]$, which show an increase of the melting point, when the alkyl chain becomes longer than the propyl chain.[5a]

While the perchlorinated $[B_{12}Cl_{12}]^{2-}$ anion decomposes above 600 °C,[1c] the thermal stability of the alkoxy-substituted anions is significantly reduced. In general the $[NBu_4]^+$ salts decompose at lower temperatures than the $[C_6mim]^+$ salts, which is exemplarily depicted for the $[B_{12}Cl_{11}O\text{-propyl}]$-anion in Fig. 2. All $[C_6mim]^+$ salts decompose above 335 °C with the exception of $[C_6mim]_2[B_{12}Br_{11}O\text{-dodecyl}]$, which decomposes at 240 °C. The mass loss of the first decomposition step is in good agreement with splitting of the alkyl group and thus breaking the oxygen–carbon bond. Combined thermo-analytical and mass spectrometric measurements (Fig. S93, S97, and S101†) show typical fragments of alkyl groups and thus also confirm the assignment of the first decomposition step to the loss of the alkyl group. The subsequent decomposition steps at higher temperatures, which are probably related to the decomposition of the cation and at even higher temperature also to the boron cluster, cannot be assigned unambiguously.

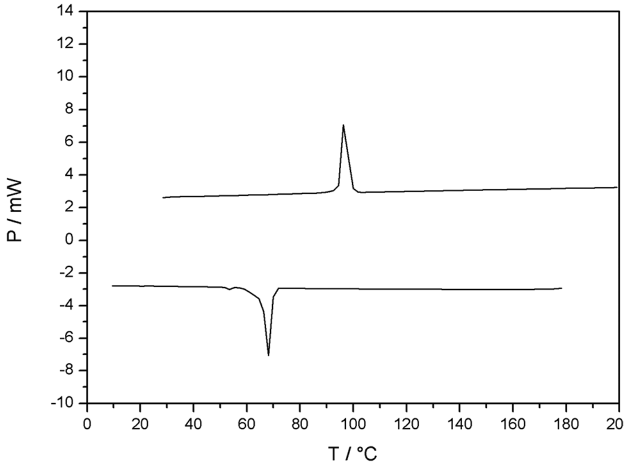


Fig. 1 Heating and cooling curves for $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ obtained by DSC.

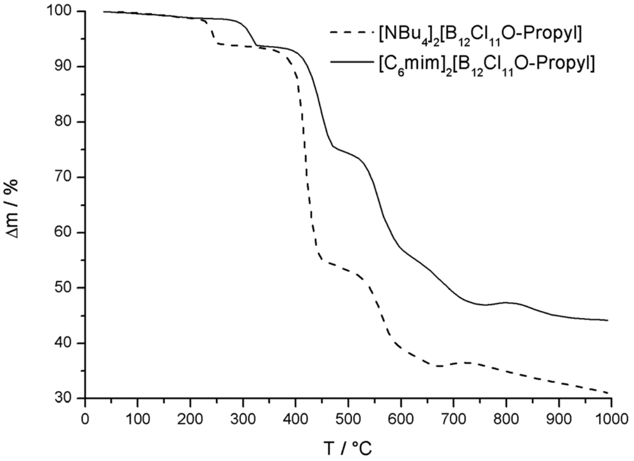


Fig. 2 Thermogravimetric analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$ and $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$.

Crystal structures

All attempts to obtain crystals suitable for X-ray diffraction of the $[NBu_4]^+$ or $[C_6mim]^+$ salts were unsuccessful. However, by using the $[PPh_4]^+$ counter cation suitable crystals were easily grown from an acetonitrile/diethyl ether solution. The crystal structures of the hydroxo clusters $[B_{12}X_{11}OH]^{2-}$ (X = Cl, Br) and the alkylated clusters $[B_{12}X_{11}OR]^{2-}$ (X = Cl, Br; R = propyl, octyl) were determined (Table 4 and Fig. 3). In the halogenated hydroxo clusters $[B_{12}X_{11}OH]^{2-}$ (X = Cl, Br) the hydroxo group is disordered over two positions (see Fig. S111 and S112 in the ESI†) which is in contrast to the ordered structure of the non-halogenated derivative $[B_{12}H_{11}OH]^{2-}$.[12] Alkylation always leads to an ordered structure. The propyl substituted clusters are independent of the halogen substituent quite similar. In contrast, the structures containing the longer octyl chain vary depending on the halogen substituent on the boron cluster. All anions show more or less pronounced C–H⋯X (X = Cl, Br) hydrogen bonds.[15] In all four structures the methylene group neighbored to the oxygen points to one halogen atom of the boron cluster in the *ortho* position. The hydrogen atoms of this methylene group show short intramolecular contacts to one or two halogen atoms. The H⋯Cl distances (273.9–291.1 pm) are shorter than the H⋯Br distances (294.2–309.5 pm). As a consequence, the B–O–C angles are smaller in the chloro derivatives (117–124°) than in the bromo derivatives (126–127°). In all structures the B–O bond is bent away from the chlorine atom, which forms the C–H⋯X contacts, indicating steric repulsion of the methylene group neighbored to the oxygen atom and the halogen atoms in the *ortho* position. The octyl chain in the structure of $[B_{12}Br_{11}O\text{-octyl}]^{2-}$ coils itself around the anion, while in the chlorinated cluster the octyl chain is pointing away from the anion. Several additional intramolecular C–H⋯Br contacts are present in the $[B_{12}Br_{11}O\text{-octyl}]^{2-}$ anion, nevertheless it remains unclear why the structures of the chloro and the bromo derivatives are so different. Additional intramolecular C–H⋯X contacts between anions

Table 4 Crystallographic parameters[a]

	$[PPh_4]_2[B_{12}Cl_{11}OH]$	$[PPh_4]_2[B_{12}Br_{11}OH]$	$[PPh_4]_2[B_{12}Cl_{11}O\text{-propyl}]$	$[PPh_4]_2[B_{12}Cl_{11}O\text{-octyl}]$	$[PPh_4]_2[B_{12}Br_{11}O\text{-propyl}]\cdot CH_3CN$	$[PPh_4]_2[B_{12}Br_{11}O\text{-octyl}]\cdot OEt_2$
Formula	$C_{48}H_{40}B_{12}Cl_{11}OP_2$	$C_{48}H_{40}B_{12}Br_{11}OP_2$	$C_{51}H_{47}B_{12}Cl_{11}OP_2$	$C_{56}H_{57}B_{12}Cl_{11}OP_2$	$C_{53}H_{50}B_{12}Br_{11}NOP_2$	$C_{60}H_{67}B_{12}Br_{11}O_2P_2$
CCDC no.	1057639	1057640	1057641	1057642	1057643	1057644
M	1214.41	1703.47	1257.50	1327.63	1787.61	1890.81
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/pm	1495.69(4)	1288.17(2)	1127.145(18)	1217.21(4)	1180.24(4)	1208.12(4)
b/pm	1015.60(3)	1234.53(2)	2847.14(5)	1649.10(5)	3885.26(14)	1699.30(5)
c/pm	1809.74(5)	1913.05(4)	3005.22(5)	1747.60(5)	1396.73(4)	1849.10(4)
α/°	90	90	113.9658(17)	93.883(2)	90	88.517(2)
β/°	100.432(2)	108.9073(19)	90.7492(14)	103.004(3)	91.786(2)	77.871(2)
γ/°	90	90	94.0845(13)	102.370(3)	90	73.201(3)
U/nm^3	2.70359(12)	2.87814(9)	8.7810(3)	3.31378(17)	6.4017(4)	3.55054(18)
Z	2	2	6	2	4	2
μ(Mo-K$_\alpha$)/mm^{-1}	0.663	7.749	0.615	0.547	6.973	6.292
No. of data collected	15 848	14 897	91 326	29 031	43 395	35 549
No. of unique data	6304	6727	40 498	12 967	15 102	16 534
R_{int}	0.0235	0.0237	0.0284	0.0404	0.0729	0.0326
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0400, 0.0924	0.0284, 0.0523	0.0661, 0.1455	0.0589, 0.1537	0.0559, 0.1347	0.0364, 0.0648
R_1, wR_2 (all data)	0.0477, 0.0964	0.0437, 0.0570	0.0927, 0.1625	0.0701, 0.1605	0.0741, 0.1471	0.0671, 0.0734

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4])^{1/2}$.

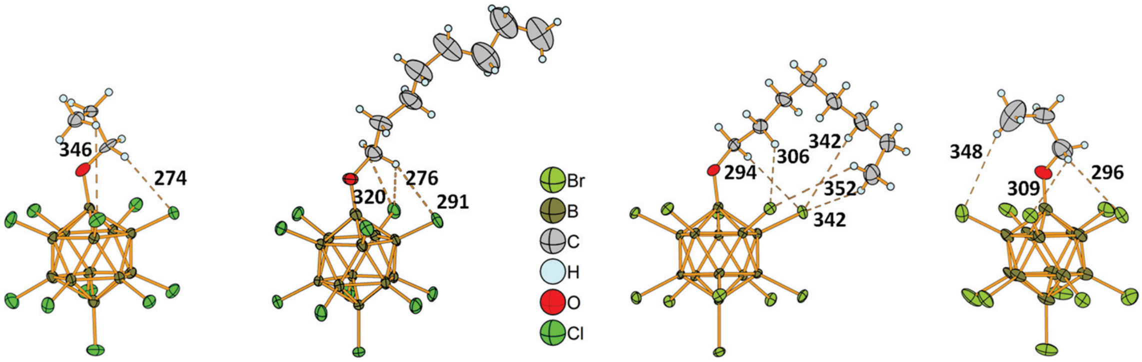


Fig. 3 Anions in the crystal structures of $[PPh_4]_2[B_{12}Cl_{11}O\text{-propyl}]$, $[PPh_4]_2[B_{12}Cl_{11}O\text{-octyl}]$, $[PPh_4]_2[B_{12}Br_{11}O\text{-octyl}]$, and $[PPh_4]_2[B_{12}Br_{11}O\text{-propyl}]$. The Cl⋯H distances are given in pm. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.

and cations are present as well in all structures, which presumably significantly determine the packing and also the orientation in space of the alkyl chains.

Conclusion

Alkoxy substituted and perhalogenated *closo*-dodecaborates were synthesized for the first time and their spectroscopic, thermal and structural properties were determined. The alkoxy groups significantly lower the melting point of their salts compared to the $[B_{12}X_{12}]^{2-}$ anions. They are still quite resistant to oxidation as determined by cyclic voltammetry (see Fig. S110†) and their decomposition temperatures are still above 300 °C (Table 3), however, they are much lower than for the perhalogenated *closo*-dodecaborate $[B_{12}Cl_{12}]^{2-}$ and 1-carba-*closo*-dodecaborate $[HCB_{11}Cl_{11}]^{-}$ anions.[1] The salt $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ has a melting point of 96 °C and thus can be regarded as an ionic liquid. Interestingly the anion carrying the quite short propyl group leads to the salt with the lowest melting point. Ionic liquids containing doubly charged anions are rare,[16,17] thus $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ is a representative of this elusive class of compounds.

Experimental section

General remarks

All solvents and the following chemicals were used as purchased from the manufacturer: $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{Br}$ (Aldrich, 99%), $[C_6mim]Cl$ (Aldrich, ≥97%), Et_3N (Riedel-de Haen), acetonitrile (Fisher Scientific), DMSO (Roth, 99.5%), *n*-propyl bromide (Sigma-Aldrich, 99%), *n*-octyl bromide (Sigma-Aldrich, 99%), *n*-dodecyl bromide (Sigma-Aldrich, 97%), KOH (Grüssing, 85%), and NaOH (Roth, ≥99%). $K_2[B_{12}H_{12}]$ was prepared by a published procedure.[9] $[B_{12}H_{11}OH]^{2-}$ was obtained from $[B_{12}H_{12}]^{2-}$ by a time and temperature controlled reaction with sulfuric acid.[12] Synthetic and spectroscopic details for the preparation of $[B_{12}H_{11}OH]^{2-}$ (X = H, Cl, Br) anions are included in the ESI.†

IR spectra were measured on a Bruker ALPHA P FT-IR spectrometer equipped with a diamond ATR attachment. Raman spectra of samples in flame-sealed capillaries were recorded using a Bruker Equinox 55 FRA 106/S FT-Raman spectrometer equipped with a highly sensitive Ge detector and a Nd:YAG-Laser (1064 nm). NMR spectra were measured on a Bruker Avance 400 and a Bruker AvanceIII 600 spectrometer in 5 mm NMR tubes at room temperature. Air and moisture sensitive samples were measured in 5 mm NMR tubes equipped with a J. Young Teflon in a glass valve. Chemical shifts are given with respect to Me_4Si (^1H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). Two dimensional NMR experiments were performed to assist the assignment of the spectra. Electrospray ionization (ESI) mass spectra were recorded using a Bruker micrOTOF instrument. Thermoanalytical measurements were done with a Mettler Toledo TGA/DSC 1 LSTAR System. The coupled thermogravimetric/mass spectrometric measurements (see ESI) were carried out with a Mettler Toledo TGA/DSC 1 LSTAR System connected to Pfeiffer Vacuum Thermostar Gas Analysis System and a Gas Controller GC 200. Melting points were measured using a Stuart SMP10 melting point apparatus.

Crystal structure determination

The $[PPh_4]^+$ salts used for diffraction experiments were synthesized by a simple metathesis reaction. 100 mg of the specific sodium salt were dissolved in 10 ml of water and a twofold molar excess of $[PPh_4]Br$ dissolved in 10 ml of water was added. After stirring for two hours the white precipitate was filtered off, washed with a small amount of cold water and dried under low pressure at 80 °C. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a solution of the respective salt in acetonitrile. The single crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini E Ultra diffractometer equipped with a 2 K × 2 K EOS CCD area detector and a four-circle kappa goniometer using MoKα (0.71073 Å) radiation at 120 K. The crystals were mounted onto a cryo loop using fluorinated oil and frozen in the cold nitrogen stream of the goniometer. Details of the crystallographic data collection and the refinement parameters can be found in Table 4. The structures were solved by direct methods (SHELXS)[18] using the program package OLEX2.[19] Subsequent least-squares refinement on F^2 (SHELXL)[18] located the positions of the remaining atoms in the electron density maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model. The data were corrected for absorption.

Synthesis of $Na_2[B_{12}X_{11}OR]$ (X = Cl, Br; R = propyl, octyl, dodecyl)

Here a general procedure is given. Yields and all spectroscopic data are included in the ESI.† 1.00 g (1.71 mmol in the case of the chloro cluster, 0.93 mmol in the case of the bromo cluster) of the specific sodium salts synthesized above was dissolved in 20 ml of DMSO. In the second step a tenfold molar excess of the alkyl bromide was added *via* a microliter syringe. After that the reaction was initiated by adding KOH (485 mg, 8.65 mmol in the case of the chloro cluster/264 mg, 4.70 mmol in the case of the bromo cluster). The colorless solutions remained colorless or turned pale yellow to yellow depending on the alkyl halide used. The mixtures were stirred at room temperature for two days. Subsequently the solutions were filtered and all volatiles were removed under low pressure and heating to 70 °C. The residue was washed with a small amount of isopropyl alcohol, filtered and dried at 120 °C.

Synthesis of $[NBu_4]_2[B_{12}X_{11}OR]$ (X = Cl, Br; R = propyl, octyl, dodecyl)

Here a general procedure is given. Yields and all spectroscopic data are included in the ESI.† 100 mg of the specific sodium salt were dissolved in 10 ml of water. A twofold molar excess of tetrabutylammonium bromide was dissolved in 10 ml of water and the two solutions were combined and stirred for two hours. The white precipitate was filtered, washed with a small amount of cold water and dried under low pressure at 80 °C.

Synthesis of [C_6mim]$_2$[$B_{12}X_{11}$OR] (X = Cl, Br; R = propyl, octyl, dodecyl)

Here a general procedure is given. Yields and all spectroscopic data are included in the ESI.† 100 mg of the specific sodium salt were dissolved in 10 ml of water. A twofold molar excess of 1-hexyl-3-methylimidazolium chloride was dissolved in 10 ml of water and the two solutions were combined and stirred for two hours. The white precipitate was filtered, washed with a small amount of cold water and dried under low pressure at 80 °C.

Acknowledgements

We are grateful to Anke Helfer, Prof. Ulrich Scherf, Philipp Hagemann, Martina Henseleit, and Prof. Roland Görtz for the thermo-analytical measurements and to the crystallographic reviewer for providing helpful advice.

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