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Phase transition investigations of closo-hydroborates

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Abstract

Decahydrodecaborates $M_2B_{10}H_{10}$ (M = Me_4N, Et_4N, Et_3NH, n-Bu_4N, Na, K) and dodecahydrododecaborates $M_2B_{12}H_{12}$ (M = Et_4N, Li) have been studied in the solid state between 200 and 400 K using DSC, XRD and ^{11}B MAS NMR techniques. Reversible phase transitions were observed with $(Et_4N)_2B_{10}H_{10}$ at 263–277 K ($\Delta H = 10.03$ kJ mol^{-1}), $(Et_3NH)_2B_{10}H_{10}$ at 324 K ($\Delta H = 15.32$ kJ mol^{-1}), $Na_2B_{10}H_{10}$ at 382 K ($\Delta H = 9.81$ kJ mol^{-1}) and $(Et_4N)_2B_{12}H_{12}$ between 200 and 220 K ($\Delta H = 3.99$ kJ mol^{-1}). The transitions were first order except for $(Et_4N)_2B_{12}H_{12}$. The well resolved signals in the MAS NMR spectra recorded at high temperature became wide quadrupolar signals at temperatures lower than the transition temperature. These results were interpreted as to be caused by changes in the motions of the hydroborate cages in the cation framework. The sharp lined MAS NMR spectra are caused by large motions of the cages which average the observed quadrupolar magnetic moments of the boron atoms. When these large motions are stopped or hindered due to a crystallographic or an order–disorder transition, the MAS NMR spectra are broadened. Attempts to determine the structure of tetraethylammonium salts probably failed because the positions of the anions in the solid are disordered even at temperatures lower than the transition temperature.

Introduction

Hydroborates have been widely studied during the last thirty years with the aim of elucidating their particular structure and investigating their properties with a view to potential applications. However the structures of the well known tetraethylammonium decahydrodecaborate and dodecahydrododecaborate have never been established although the great stability of these compounds allows all the classical methods of crystallographic investigations [1–4]. In the earliest attempts to determine the boron cage shape and the boron–boron distances, hydrated $K_2B_{10}H_{10}$ or $(Me_4N)_2B_{10}H_{10}$ was used, but the crystallographic calculations permitted only the unit cell and space group determinations [1]. The choice of the copper derivative, $Cu_2B_{10}H_{10}$, for the determination of the structure of the $B_{10}H_{10}^{2-}$ anion by Dobrott and Lipscomb is clearly explained [1]: with this salt the refinements calculation could be resolved and the structure elucidated. More recently the structures of other decahydrodecaborates and dodecahydrododecaborates have been determined using various types of cations associated to the boron cage: (i) heavy alkaline (K^+, Rb^+) or alkaline earth (Sr^{2+}) cations [5–7], (ii) symmetric $(PPh_3)_2Cu^+$ [8] or unsymmetric $Et_2FeNRMe^+$ [9–12] bulky cations and (iii) hydrated cations such as Ca^{2+} or Mg^{2+} [13]. In some cases hydration facilitates the study of salts containing small cations; a similar effect, which could explain the XRD data of hydrates of the acids $H_2B_{12}X_{12}$ (X = Cl, Br, I), was determined [14]. In the same way the temperature dependence of XRD properties of $Na_2B_{12}H_{12}\cdot 4H_2O$ has been studied [15] but much fewer diffraction lines were observed. More recently the B_{12} cage structure was determined using the salt $(Et_3NH)_2B_{12}H_{12}$ [16] which contains a bulky asymmetric cation.

The ^{11}B chemical shifts of crystallized hydroborates measured by MAS NMR have been previously reported [17]. The two main conclusions reached were: (i) very few changes in the ^{11}B chemical shifts are observed between solid state and solution when the spectra are well resolved and (ii) the high resolution spectra are always obtained with tetraalkylammonium salts whereas anhydrous alkaline cations do not lead to very sharp resonance peaks.

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It has already been observed that the nature of the cation affects the NMR properties of solid octahydrotriborates [18, 19] and that there is a correlation between phase transition, the cation size and the resolution of the MAS NMR spectra related to wide angle motions [20].

The purpose of the present work was to find if there is a relation between the properties of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ salts determined by DSC, XRD, MAS NMR and the motions in the solid.

Experimental

Materials

The hydroborate(−2) salts were obtained by pyrolysis of Et_4NBH_4 using known methods of synthesis and separation [21]. The purification of the tetraakylammonium salts was carried out by HPLC. For cation exchanges, the tetraethylammonium salt was first converted to the corresponding acid by percolation through a cationic resin (Duolite 20 H) charged with protons. The diluted acidic solution was then neutralized using the appropriate hydroxide under pH control. The different salts were recovered from the solution by evaporation and usually recrystallized from acetonitrile solution. The drying of the salts was performed under low pressure (about 10^{-4} mbar) at 120 °C for several hours. Their purity was better than 99% (^1H, ^{13}C and ^{11}B NMR determinations).

DSC (differential scanning calorimetry)

A Mettler 2000B DSC was used to determine the temperature and the transition enthalpies. The sample mass was about 10 mg, and generally a 5° per minute heating rate was used.

MAS NMR measurements (magic angle spinning nuclear magnetic resonance)

^{11}B MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer equipped with a double bearing MAS probe-head operating at 96.25 MHz. Chemical shifts were referenced to external $B(OMe)_3$. The hydroborate salts were placed directly in the small zirconia rotor. The boron nitride bottom of the commercial rotor was replaced by a teflon stopper specially for broad band spectra recording. The rotor was spun at about 4 kHz during the spectral recording. Very short radio-frequency pulses (2 μs) were used to get comparable signals as described previously [17, 22]. The spectra were usually obtained after 100 scans with one second delay between each scan. The sample was cooled using a cooling gas (N_2) whose temperature was measured during the spectra recording. The lowest temperature reached was 200 K.

XRD determinations (X-ray diffraction)

These measures were performed using a Philips generator and goniometer equipped with an Anton Paar low temperature sample chamber operating under controlled atmosphere.

Results

Thermal behaviour — DSC studies

The thermal behaviour of the hydroborate salts was studied from 200 to 400 K. The enthalpies and the temperatures of the transitions are given in Table 1.

The observed phase transitions do not present a very sharp endotherm as expected for first order simple transitions. The DSC curves recorded under the same conditions (sample weight, heating rate, sensitivity of the apparatus) for all the compounds having phase transitions are given in Fig. 1. The transition phenomena are spread over a large temperature range as high as 40 °C for $Na_2B_{10}H_{10}$.

Among the tetraalkylammonium decahydrodecaborates, only the tetraethylammonium salt exhibits a phase transition which is not a simple first order transition, the DSC and calorimetric curves showing two steps [23]. The enthalpies of the complex transitions observed

TABLE 1. DSC determinations of temperatures and enthalpies of the transitions in some hydroborates

$B_{10}H_{10}^{2-}$ salts associated cation	Temperatures of transitions (K)	Enthalpy	
		kJ mol^{-1}	J g^{-1}
Me_4N^+	no transition		
Et_4N^+	263/277	10.0	26.5
Et_3NH^+	324	15.3	47.5
$n\text{-}Bu_4N^+$	no transition		
Na^+	382	9.81	59.9
K^+	*no transition*		
$(Et_4N)_2B_{12}H_{12}$	225/231/235	3.99	10.2

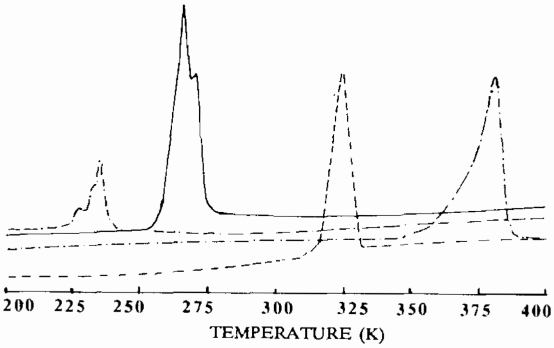

Fig. 1. DSC recording of the transitions in the hydroborates: – – – $(Et_3NH)_2B_{10}H_{10}$, — · – $Na_2B_{10}H_{10}$, —— $(Et_4N)_2B_{10}H_{10}$, – – · – $(Et_4N)_2B_{12}H_{12}$.

with the decahydrodecaborates salts are similar per $B_{10}H_{10}^{2-}$ unit. No transition was observed with $(n\text{-}Bu_4N)_2B_{10}H_{10}$, $K_2B_{10}H_{10}$ and $(Me_4N)_2B_{10}H_{10}$ between 200 and 400 K.

For $(Et_4N)_2B_{12}H_{12}$, the energy of 3.99 kJ mol^{-1} corresponds to a second order transition including crystallographic and order–disorder phenomena.

Studies by ^{11}B MAS NMR

Influence of the cation associated to $B_{10}H_{10}^{2-}$

The general shape of the ^{11}B MAS NMR spectra obtained with hydroborates depends upon the associated cation. Using tetraalkylammonium salts, the $^{11}B\{^1H\}$ spectra can be compared with solution spectra but with alkaline cations, the spectra exhibit mainly a broad signal (about 10 kHz at 96.25 MHz). For the sharp lined spectra, the chemical shifts and the linewidth measured at room temperature are given in Table 2. In spite of the quadrupolar nuclear moment of the ^{11}B nucleus, a very precise resolution is obtained with tetraalkylammonium salts with a ^{11}B linewidth of $\Delta\nu_{1/2} = 120$ to 150 Hz upon ^1H decoupling. The good resolution of the MAS NMR spectra of $(Et_4N)_2B_{10}H_{10}$ in the solid state was attributed in previous work [20] to the anion–cation interaction and the size of the cation which allow large angle internal motions averaging the quadrupolar interactions around the ^{11}B nucleus.

There is only a very small variation of the ^{11}B chemical shift as a function of the tetraalkylammonium salts. However the linewidths are different but no correlation could be established between the cation size and the resolution; Et_4N^+ salts always show the sharper spectra.

Proton coupling effect

The proton coupling effect is rather important, especially when the spectra exhibit sharp resonance lines or at a temperature just below the transition where only the decoupled spectrum exhibits the two resonance peaks corresponding to the two types of boron atoms of the cage as shown in Fig. 2 for $(Et_3NH)_2B_{10}H_{10}$. The resonance peak of the two apical boron atoms rises then from the broad band whereas the resolution of the coupled signal is very bad. A similar effect has been observed with $Na_2B_{10}H_{10}$ at room temperature. When the coupled spectra exhibit a poor resolution, for instance with $K_2B_{10}H_{10}$, the proton decoupling effect is less efficient and the band narrowing is only 1 kHz.

Temperature variation effects

The important differences observed between the MAS NMR spectra of hydroborates can be explained in terms of interaction between anion and cation. In a previous study [20] carried out on $Me_4NB_3H_8$, the variation of the $^{11}B\{^1H\}$ spectra with the temperature has shown a linewidth broadening from 120 Hz at room temperature to 6.5 kHz when the temperature was lower than the temperature of transition. Owing to the existence of a crystallographic transition in $(Et_4N)_2B_{10}H_{10}$ at easily obtainable temperatures NMR spectra were recorded at temperatures just below and above the transition temperature. The $\{^1H\}$ decoupled MAS NMR spectra of $(Et_4N)_2B_{10}H_{10}$ were recorded at decreasing temperatures; the broadening of the two sharp lines is shown in Table 3.

When the sample was cooled, in a first step, only the linewidths increased. While this broadening occurred, a very large signal (linewidth 30 kHz) began to appear. It was not possible to determine the relative

TABLE 2. $\delta^{11}B$ (Ref $B(OMe)_3$) and half-width of the ^{11}B MAS NMR lines in hydroborates at room temperature

$B_{10}H_{10}^{2-}$ salts cation	Apical boron atoms			Equatorial boron atoms		
	$\delta^{11}B$ (ppm)	$\Delta\nu_{1/2}$ (Hz)		$\delta^{11}B$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	
		$\{^1H\}$ dec	$\{^1H\}$ coup		$\{^1H\}$ dec	$\{^1H\}$ coup
Me_4N^+	−20.3	320	[a]	−48.0	490	[a]
Et_4N^+	−19.5	120	210	−47.8	225	330
$n\text{-}Bu_4N^+$	−20.5	320	[a]	−50.0	780	560
Et_3NH^+				Broad peak at room temperature with two sharp lines		
Na^+				Broad band at room temperature (10 kHz) with two sharp lines		
K^+				Broad band at room temperature 11 kHz		

$B_{12}H_{12}^{2-}$ cation	$\delta^{11}B$ (ppm)	$\Delta\nu_{1/2}$ (Hz) $\{^1H\}$ dec	$\{^1H\}$ coup
Et_4N^+	−34.3	130	250
Li^+	Broad band at room temperature	14 kHz	

[a] Too poor resolution of the spectra for measurements.

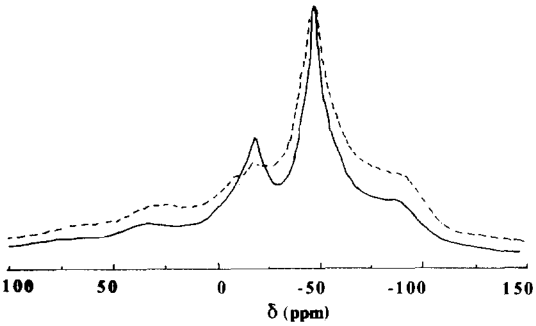

Fig. 2. {^1H} coupling effect on $(Et_3NH)_2B_{10}H_{10}$ ^{11}B MAS NMR spectra at room temperature: —— {^1H} decoupled, - - - - {^1H} coupled.

TABLE 3. Linewidth variations with temperature lowering in $(Et_4N)_2B_{10}H_{10}$

Temperature (K)	$\Delta\nu_{1/2}$ (Hz) for boron	
	Apical	Equatorial
300	225	330
273	225	340
253	230	500
233	600	690
213	990	830
198	broad band	

proportions of fine and broad signals because the relative surface area of these signals can be modified by more than one order of magnitude depending on the base line and phase corrections. However at 213 K, the sharp peaks were always visible but their area corresponds to only 10% of the total boron atoms. Then, when the temperature decreased, in a few degrees, the sharp peaks faded and the signal became very broad (half-width 1.4 kHz) characteristic of a complex quadrupolar signal. The spectra recorded at 300 and 198 K are shown in Fig. 3. The behaviour of $Na_2B_{10}H_{10}$ and $(Et_3NH)_2B_{10}H_{10}$ was similar; the broad band spectra obtained at room temperature turned to two sharp resonance line spectra at 373 K. It is worth noting that the important difference between the temperature of a transition measured by the spectroscopic and the thermic methods is related to technical considerations: only the temperature of the cooling gas was measured during the MAS NMR measurements and not the temperature of the sample itself.

XRD determinations

When the X-ray diffraction pattern of $(Et_4N)_2B_{10}H_{10}$ was recorded, the very few lines obtained from so complex a compound led to a difficult question. How can this salt having 28 non-hydrogen atoms per molecular unit exhibit only 5 main diffraction lines between $d = 8.9$ and 2.25 Å (Table 4).

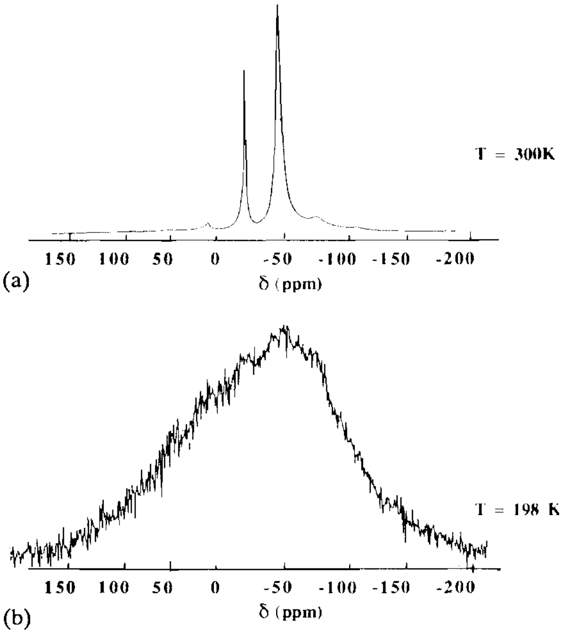

Fig. 3. Changes in the $^{11}B\{^1H\}$ MAS NMR spectra of $(Et_4N)_2B_{10}H_{10}$ with the temperature: (a) $T = 300$ K; (b) $T = 198$ K.

Another surprising feature is that the same lines are observed with $(Et_4N)_2B_{12}H_{12}$ and with $(Et_4N)_2B_{10}H_{10}$. When an $(Et_4N)_2B_{10}H_{10}$ sample is cooled, no important change (only a very small linewidth growth) can be noted on the XRD patterns until the transition temperature is reached. Then, as with the MAS NMR, in a few degrees, the pattern changes are very pronounced. However, the XRD pattern of the low temperature phase of $(Et_4N)_2B_{10}H_{10}$ always exhibits the same main lines as the high temperature phase, but they are split by a loss of symmetry. Beside these lines several new diffraction lines appear especially to the large angles. The room temperature pattern of $(Et_3NH)_2B_{10}H_{10}$ shows a similar group of main lines but with this compound, as with the low temperature phase of $(Et_4N)_2B_{10}H_{10}$, many diffraction lines can be easily measured. A comparison can be made with other tetraalkylammonium salts especially $Et_4N(FeCl_{4-n}Br_n)$ [28] where the same four first lines are visible on $Et_4N(FeCl_4)$ and where other lines appear when the anion $(FeCl_{4-n}Br_n)^-$ becomes larger and unsymmetric ($n = 1$ or 2). The diffraction patterns of $(Et_4N)_2B_{10}H_{10}$ and $(Et_4N)_2B_{12}H_{12}$ seem to be composed of the diffraction lines of the motionless cations building a rigid framework in which the anion cages move enough to be undetectable.

Discussion

The broad band observed on NMR spectra at a lower temperature than the temperature of transition is consistent with the resonance of quadrupolar boron atoms

TABLE 4. XRD data for some alkylammonium hydroborates at 25 °C and the low temperature phase of $(Et_4N)_2B_{10}H_{10}$

$(Et_4N)_2B_{12}H_{12}$		$(Et_4N)_2B_{10}H_{10}$		Low temperature $(Et_4N)_2B_{10}H_{10}$		$(Et_3NH)_2B_{10}H_{10}$	
I	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)
75	8.15	60	8.07	50	7.97	80	7.97
				15	7.31	20	7.56
30	7.10	50	6.99	30	7.08	40	6.70
				1	5.50	10	5.37
				65	5.03	20	4.94
100	5.05	100	4.98	100	4.84	100	4.72
						16	4.51
30	4.30	50	4.24	50	4.23	30	4.34
3	4.14	3	4.09	30	4.02	40	4.14
3	4.11	3	4.05			21	4.00
						20	3.73
						20	3.70
2	3.56	3	3.53	3	3.53		
6	3.29			3	3.30		
17	3.26	18	3.23	10	3.24		
1	3.18			16	3.18	11	3.17
						8	3.11
				13	2.840	8	3.00
1	2.754	1	2.74				
2	2.738	1	2.698				
				8	2.644	5	2.682
				5	2.488		
2	2.404	1	2.367	8	2.410		
2	2.373	1	2.332	9	2.338		

in crystallographic sites producing an anisotropic effect. An example of a complex spectrum has been described with boron oxide glasses [25] and is composed of the sum of two signals, a sharp signal (4 kHz) which corresponds to the tetracoordinated borons and a broad (16 kHz) complex quadrupolar signal due to tricoordinated boron atoms. In hydroborates, the boron atom surrounding is assumed to induce an anisotropy which makes most boron atoms of the cage different from their neighbours. The ^{11}B NMR spectrum corresponds to the sum of all the components, each inequivalent boron giving an about 10 kHz quadrupolar signal as mentioned for $Me_4NB_3H_8$ and KB_3H_8 [18]. Even using MAS NMR, the resonance peaks are too broad to distinguish the different boron sites. The narrowing leading to good resolution spectra is attributed to intracrystalline motions involving the cages. These motions can be large angle motions or very fast wobbling of the $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ cage in the cation framework. Such motions already described for octahydrotriborates [18, 19] average the quadrupolar ^{11}B interaction leading to spectra with sharp signals. These peaks are obtained when the sizes of the anion and the cation are about the same [3, 24]. For $(Et_4N)_2B_{10}H_{10}$, the difference between the spectra recorded just below or just above the temperature of the transition are characteristic of the hinderance of the motion of the anion. The changes in this motion led to a classic behaviour of the boron atoms with a second order quadrupolar powder pattern [18].

Intramolecular exchanges affect the NMR properties of the $B_3H_8^-$ anion in solution [3, 26] but they must be related to the special configuration of this anion. Moreover they produce a continuous variation of the properties [27] which cannot be related to the abrupt changes observed at the phase transitions of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ salts.

The averaging of the quadrupolar moment by intracrystalline motions has been described for another family of boron–hydrogen clusters having the same icosahedral structure as $B_{12}H_{12}^{2-}$, the $C_2B_{10}H_{12}$ carboranes. Molecular motions in carboranes have been studied using NMR, DSC and XRD techniques [29–32]. Correlation between the NMR spectra characteristics, the relaxation time of ^{11}B and ^{1}H with regard to the phase transitions in the *o*-carborane has been widely discussed. Using ^{11}B and ^{13}C MAS NMR, an important difference has been observed between the spectra of unsubstituted carboranes which exhibit very sharp resonance peaks (60 to 100 Hz at 96.25 MHz) and phenyl-*o*-carborane whose signal is 1 kHz broad. The resolution of the spectra was attributed to internal motions in these compounds. In hydroborates, electrostatic fields created by the ionic charges lead to more complex systems and large motions of the anionic cages seem to require several conditions.

(i) The crystallographic site should be as symmetric as possible. In this case, the X-ray pattern of the compounds in which the motions are important exhibit only very few lines which correspond to the cation framework.

(ii) The cation and the anion should have about the same size and shape. Tetraalkylammonium cations are easily represented with a spherical symmetry [24], the electric charge carried by the nitrogen atoms being screened by the alkyl groups. However, bulky cations are often used in structure determination, but they should preferably be unsymmetric.

(iii) The electric field created by the cation should be as small as possible to lower the interaction with the cage.

These considerations lead to a good explanation of the poor results obtained by crystallographic determination [1]. For the large cations, the anion could be described in random positions in the cation framework and no fixed position can be given to the boron part of the compound. For $(Et_4N)_2B_{10}H_{10}$, when the ^{11}B MAS NMR signal exhibited a broad band, the structure could not be resolved and could be correlated with the possibility for the $B_{10}H_{10}^{2-}$ cages to 'freeze' in the cation sites. These comments are consistent with the results published on the structure of hydroborates where bulky unsymmetric cations were used to lower the symmetry of the sites [6, 7] and where the diffraction patterns obtained from complex compounds like $(Et_4N)_2B_{10}H_{10}$ and $(Et_4N)_2B_{12}H_{12}$ are very simple.

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