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Thermal, structural and possible ionic-conductor behaviour of $CsB_{10}CH_{13}$ and $CsB_{11}CH_{12}$

A.M. Romerosa

Departamento de Química Inorgánica, Facultad de Ciencias Experimentales de Almería, Universidad de Granada. La Cañada de San Urbano s/n, 04071 Almería (Spain)

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Abstract

Thermal and structural studies of the salts $CsB_{10}CH_{13}$ and $CsB_{11}CH_{12}$ in the temperature intervals 20–200 and 20–320°C respectively are reported. Comparison of these compounds to the salt $CsB_9C_2H_{12}$ in the temperature range 20–250°C suggests their ionic behaviour and the notable influence in this of the geometrical form of the various carborane anions.

INTRODUCTION

Some solids show an abnormally high ionic conductivity and are called solid electrolytes. In their crystal structure one part generally remains rigid and another is highly disordered. This disorder can be induced thermally.

Two types of thermally induced solid electrolytes can be distinguished [1–3]: those in which the disorder appears gradually with increasing temperature (CaF_2-type) and those in which appearance of disorder is associated with a phase transition (AgI-type), which can be easily identified by thermal techniques.

Recently, the new one-dimensional solid electrolyte $CsB_9C_2H_{12}$ [4] has been introduced, in which the disorder is associated with a phase transition (AgI-type). Because the geometrical form and the charges of the $[B_{10}CH_{13}]^-$ and $[B_{11}CH_{12}]^-$ anions are the same as for $[B_9C_2H_{12}]^-$, thermal and crystallographic studies of the respective Cs salts have been obtained and compared to the $CsB_9C_2H_{12}$ salt, to determine their possible ionic-conductor behaviour.

EXPERIMENTAL

$CsB_{11}CH_{12}$ and $CsB_{10}CH_{13}$ were synthesized according to Knoth [5]. The precipitate was filtered out in air and recrystallized from hot water. The subsequent analyses and spectroscopic results are in agreement with the literature data for this compound.

Differential scanning calorimetry (DSC) measurements were done on a DSC2 Perkin-Elmer automated analyser system in Ar atmosphere (heating rate = 20 K min^{-1}). Powder diffraction patterns at 26° and 202°C for $CsB_{11}CH_{13}$ and 26°, 220° and 310°C for $CsB_{11}CH_{12}$ were collected in air on a temperature-controlled attachment on a conventional Siemens D500 diffractometer using monochromatized CuKα radiation (measured 2θ range 5–50°, step size $2\theta = 0.02°$, integration time 10 s). The unit cell indexing was performed with the program TREOR. Owing to the large volume increase associated with the polymorph transition, the sample tends to arch in the sample holder. To compensate for this a zero shift parameter was also included in the refinement of the unit cell parameters.

RESULTS AND DISCUSSION

$CsB_{10}CH_{13}$

Figure 1 shows the DSC spectrum in the temperature interval 26–352°C. It indicates the existence of two consecutive broad endothermic peaks. The first peak ranges from 164 to 182°C with the maximum at 173.7°C (enthalpy of transition 3.21 kJ mol^{-1}; entropy of transition 7.29 J mol^{-1} K^{-1}), the second peak ranges from 182 to 197°C with the maximum at 185°C (enthalpy of transition 2.43 kJ mol^{-1}; entropy of transition 5.30 J mol^{-1} K^{-1}). Two phases are clearly defined: the β polymorph in the temperature interval 26–174°C and the α polymorph up to 185°C. The β polymorph was determined from a single-crystal [6] and the α polymorph was characterized by X-ray powder diffraction.

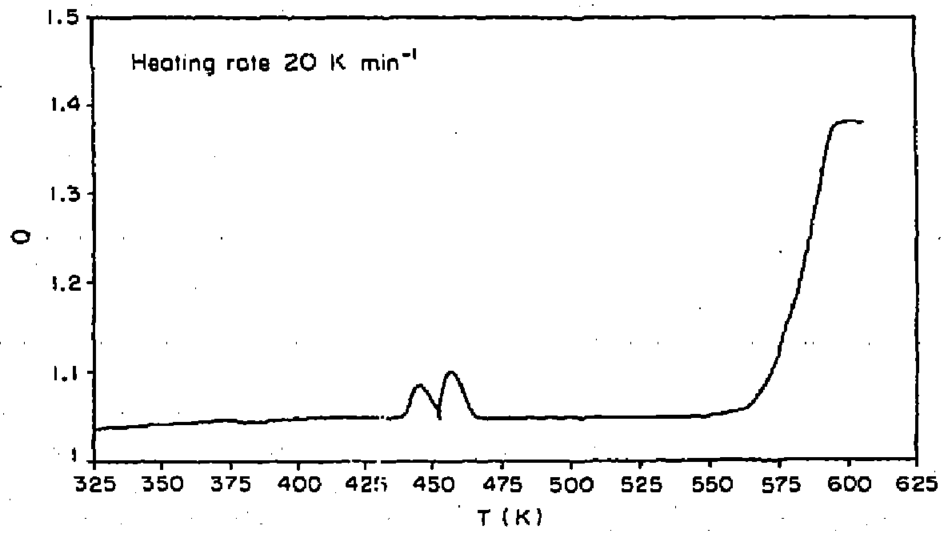

Fig. 1. DSC spectrum of $CsB_{10}CH_{13}$ in the temperature interval 26–352°C.

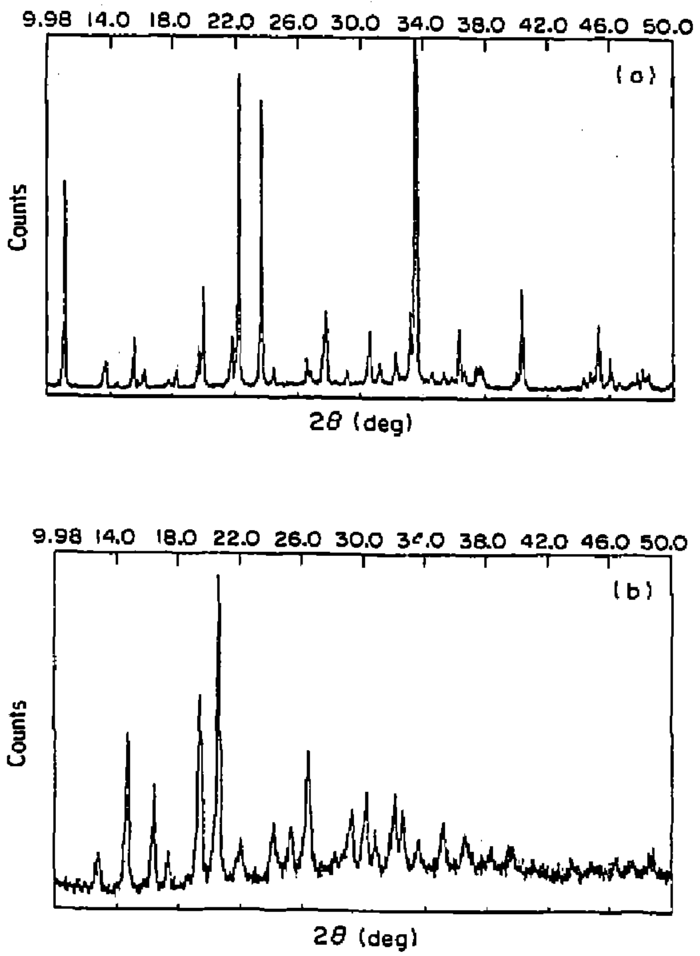

Fig. 2. Powder X-ray diffraction patterns of the β polymorph at 157°C (a) and the α polymorph at 202°C (b).

Figure 2 shows the results of the powder X-ray diffraction of β (157°C) (a) and the α (202°C) (b) polymorphs of $CsB_{10}CH_{13}$. The β phase (monoclinic $P2_1$, $a = 6.089(3)$ Å, $b = 10.638(3)$ Å, $c = 7.995(3)$ Å, $\beta = 92.50(2)$, $V = 517.4(3)$ Å^3) shows that the coordination polyhedron of Cs^+ is prismatic bipyramidal.

On the basis of 16 observed lines the α polymorph is probably monoclinic ($a = 12.146(25)$ Å, $b = 8.629(9)$ Å, $c = 11.70(2)$ Å, $\beta = 93.80(7)$, $V = 1224$ Å^3).

$CsB_{10}CH_{13}$ is similar to $CsB_9C_2H_{12}$ [4], whose α polymorph shows ionic conductivity. The volume of this conducting phase is 1066 Å^3, 158 Å^3 smaller than the volume of the α polymorph of $CsB_{10}CH_{13}$, indicating that this polymorph is more ordered than the α-$CsB_9C_2H_{12}$. The transition enthalpy of $\beta \rightarrow \alpha$ $CsB_{10}CH_{13}$ is 5640 J mol^{-1}, i.e. 9165 J mol^{-1} smaller than for the $\gamma \rightarrow \alpha$ $CsB_9C_2H_{12}$ transition, which suggests that the $\beta \rightarrow \alpha$ transition of $CsB_{10}CH_{13}$ does not involve any great disorder in the structure of this salt.

According to this it may be assumed that the α polymorph of $CsB_{10}CH_{12}$ probably does not show ionic conductivity.

$CsB_{11}CH_{12}$

The DSC spectrum of $CsB_{11}CH_{12}$ in the temperature interval 26–427°C (Fig. 3) indicates the existence of two sharp endothermic peaks. The first peak in the temperature range 131–144°C with the maximum at 137°C (enthalpy of transition 76.7 J mol^{-1}; entropy of transition 0.18 J mol^{-1} K^{-1}). The second peak in the range 277–302°C with the maximum at 291°C (enthalpy of transition 1450 J mol^{-1}; entropy of transition 2.57 J mol^{-1} K^{-1}).

In the polymorph in the temperature interval 26–137°C (the γ polymorph) there is one water molecule per anion. This phase has been determined by single-crystal X-ray diffraction data [6]. (Trigonal, R3, $a = b = 20.969(2)$ Å, $c = 13.245(3)$ Å, $V = 5043.47(1)$ $Å^3$.) The coordination polyhedron of Cs^+ is an octahedron and the water molecule is located in the 3 axis.

Figure 4 shows the X-ray powder diffractions for the β polymorph (220°C) (a) and the α polymorph (310°C) (b).

At 137°C the water molecule is eliminated, leading to the observed $\gamma \rightarrow \beta$ transition. The β polymorph is stable in the temperature interval 137–291°C.

The α phase (stable above 291°C) is probably orthorhombic ($a = 14.493(6)$ Å, $b = 12.277(5)$ Å, $c = 7.795(4)$ Å, $V = 1387.11$ $Å^3$) (indexes, Table 1).

The enthalpy of the $\beta \rightarrow \alpha$ $CsB_{11}CH_{12}$ transition (14 278 J mol^{-1}) is smaller than the $\gamma \rightarrow \alpha$ $CsB_9C_2H_{12}$ transition and the volume of the α polymorph of the $CsB_{11}CH_{12}$ is 321.4 $Å^3$ greater than α-$CsB_9C_2H_{12}$, which

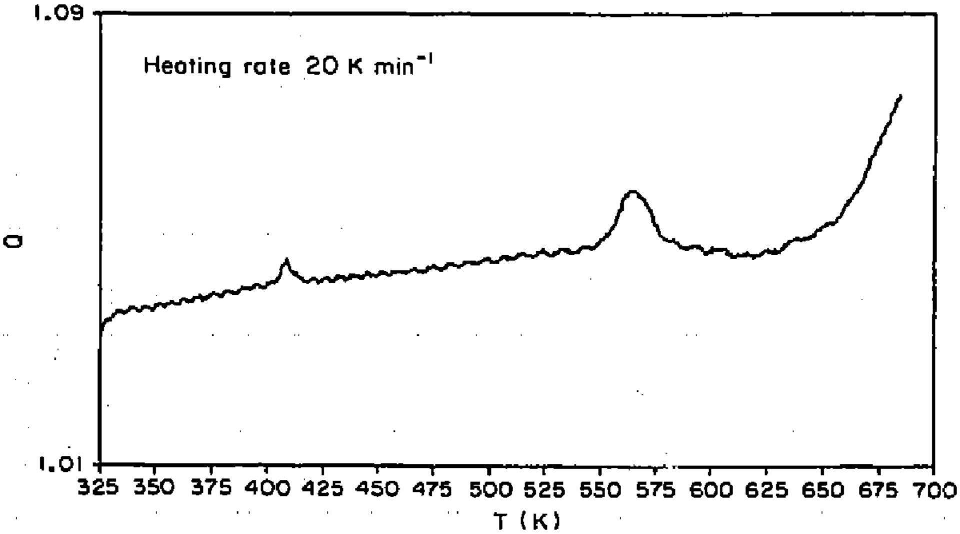

Fig. 3. DSC spectrum of $CsB_{11}CH_{12}$ in the temperature interval 26–427°C.

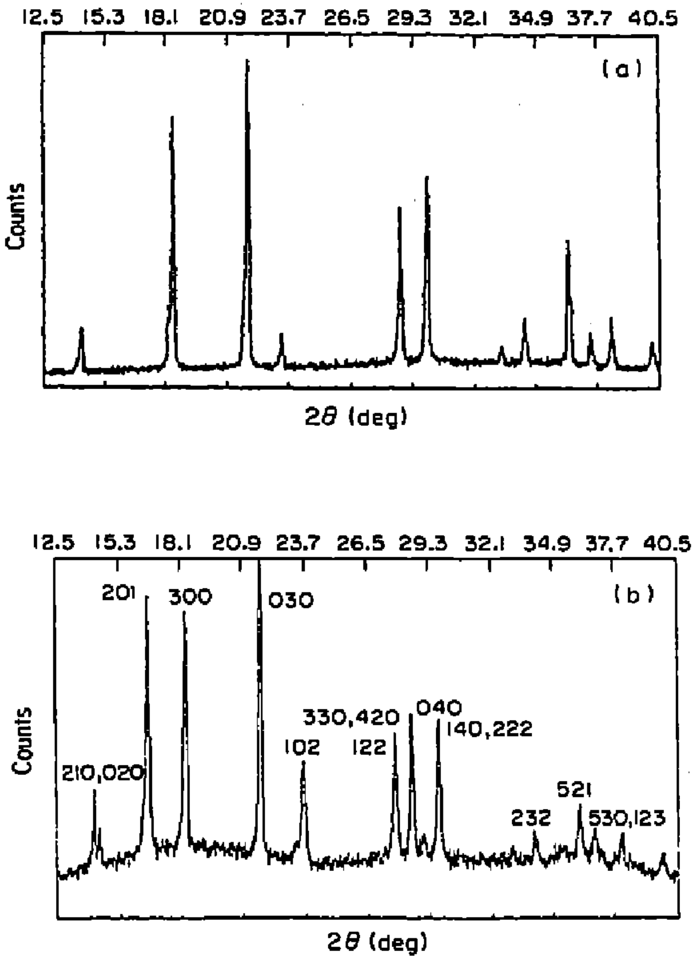

Fig. 4. Powder X-ray diffraction patterns of the β polymorph at 220°C (a) and the α polymorph at 310°C (b).

TABLE 1

X-ray powder diffraction of $CsB_{11}CH_{12}$ (310°C) indexed assuming an orthorhombic cell[a]

hkl	$1/d^2_{obs}$	$1/d^2_{calc}$	Δ	I_{meas}
210	0.0152	0.0152	−0.0000	27
020	0.0157	0.0157	−0.0000	13
201	0.0210	0.0206	−0.0000	84
300	0.0254	0.0254	−0.0001	79
030	0.0355	0.0354	0.0000	100
102	0.0419	0.0419	0.0000	34
122	0.0576	0.0576	0.0000	41
330, 420	0.0608	0.0608	0.0001	46
040	0.0629	0.0630	0.0000	8
140, 222	0.0658	0.0658	0.0000	45
232	0.0860	0.0858	0.0002	12
521	0.0961	0.0961	0.0000	18
530, 123	0.1063	0.1064	0.0002	11

[a] Refined cell parameters: $a = 14.493(6)$ Å; $b = 12.276(5)$ Å; $c = 7.796(4)$ Å.

suggests that α-$CsB_{11}CH_{12}$ is more ordered than α-$CsB_9C_2H_{12}$ and probably shows no ionic conductivity (like the $CsB_{10}CH_{13}$ salt).

CONCLUSIONS

$CsB_{10}CH_{12}$, $CsB_{11}CH_{12}$ and $CsB_9C_2H_{12}$ salts are anions with radii of similar order and the same charge. The $CsB_9C_2H_{12}$ is a Cs^+ ionic conductor but $CsB_{10}CH_{13}$ and $CsB_{11}CH_{12}$ are not ionic conductors. This result shows that salts with monovalent anions in which the cation/anion radii ratio is about 0.5 (0.58, AgI; 0.49, CsB_9CH_{12}) probably show ionic conductivity but other effects in the structure of solid ionics also have influence.

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