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Xu, Y., Reinholdt, A., Antzutkin, O. et al (2024). Ionic Interaction Effects on the Structure and Dynamics of Orthoborate Ionic Materials. Crystal Growth & Design, 24(21): 8989-8998. http://dx.doi.org/10.1021/acs.cgd.4c01030

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Article

Ionic Interaction Effects on the Structure and Dynamics of Orthoborate Ionic Materials

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Cite This: Cryst. Growth Des. 2024, 24, 8989–8998



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ABSTRACT: A series of orthoborate-based ionic materials of bis(glycolato)borate ([BGB]) and bis(ethylene-1,2-dioxy)borate anions ([BEDB]) coupled with tetrabutylphosphonium ([P₄₄₄₄]) and tetrabutylammonium ([N₄₄₄₄]) cations have been synthesized, and their physicochemical properties are characterized. The ionic materials based on the most popular orthoborate anion, bis(oxalato)borate anion ([BOB]), which contains four carbonyl groups, are all liquid at ambient temperature, while the bis(glycolato)borate ([BGB]) anion, with two carbonyl groups, and the bis(ethylene-1,2-dioxy)borate ([BEDB]) anion, without carbonyl groups, render solids at ambient temperature. The ionic materials based on the [BGB] anion display the highest decomposition temperatures, and those based on the BEDB anion are the lowest. The [P₄₄₄₄][BGB], [P₄₄₄₄][BEDB], and [N₄₄₄₄₁][BEDB] salts feature significantly wider plastic phase I temperature ranges than their analogues. FTIR spectroscopy, multinuclear (¹⁵N, ³¹P, ¹³C, and ¹¹B) solid-state NMR spectroscopy, and single-crystal X-ray diffraction were all used to unveil the ionic



interactions and structural features, which display weaker ionic interactions for [BEDB] compared to [BGB] when bearing the same cation and present relatively higher crystallinity of $[P_{4444}][BGB]$ among the ionic materials.

INTRODUCTION

Boron compounds and boron-based salts have promising properties suited for many application areas such as lubrication,¹ pharmaceutics,² electronics,³ and energy storage.⁴ As for medicinal use, the U.S. FDA in 2003 approved the first proteasome inhibitor bortezomib, for treating multiple myeloma that contains boron⁵ (PS-341 or Velcade). Boron-containing polymers can provide advanced features including lightweight, high melting point, flexibility, etc. for electronic applications,³ and in the context of energy storage applications, boron compounds provide distinctive benefits for enhanced performance in battery applications, as various novel anionic boron clusters and boron-containing solid materials have been proposed as components of novel electrolytes, potentially replacing conventional electrolytes.^{6–12}

Among solid-state materials for energy applications, organic ionic plastic crystals (OIPCs) have emerged as attractive solidstate electrolytes (SSEs) for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) and have been widely studied over the past decade.^{13–18} Similar to room-temperature ionic liquids (RTILs), OIPCs possess a combination of highly wanted electrolyte properties including nonvolatility, nonflammability, high thermal stability, high ionic mobility, and structural designability. This makes the OIPCs strong SSE candidates. In addition, the increased disorder and defects present in OIPCs at elevated temperatures provide plasticity and enhanced diffusion, improving the ionic conductivity.¹⁹ This is important and a challenge as in contrast to RTILs that have ionic conductivities in the range from 10^{-4} to 10^{-3} S cm⁻¹ at ambient temperature,^{20,21} OIPCs still have too low ionic conductivities, for example, battery application.¹⁶

Most of the reported OIPCs are based on heavily fluorinated anions such as bis(fluorosulfonyl)imide ([FSI]),²² bis-(trifluoromethanesulfonyl)imide ([TFSI]),²³ hexafluorophosphate $([PF_6]^-)$,²⁴ and tetrafluoroborate $([BF_4]^-)$.²⁵ By employing a halide-free synthesis route, Kang et al.²⁶ created OIPCs with the new difluoro(oxalato)borate ([DFOB]) anion coupled with either triethylmethylammonium $([N_{1222}])$ or 1-ethyl-1methylpyrrolidinium $([C_2mpyr])$ cations, which showcased combined benefits of good solid electrolyte interphases (SEIs), Al corrosion inhibition, high salt solubility, and nonflammability. Yunis et al.²⁷ synthesized a series of N,N-diethylpyrrolidinium $([C_2epvr])$ cation-based RTILs and plastic crystals; the RTILs were formed when the cation was combined with fluorosulfonyl-(trifluoromethanesulfonyl)imide ([FTFSI]) and dicyanamide ([DCA]) anions, while OIPCs were obtained when coupled to [TFSI], [FSI], $[PF_6]^-$, and $[BF_4]^-$ anions. The OIPCs displayed beneficial thermal and transport properties, and the [C₂epyr]-[FSI] exhibited an ionic conductivity of 1.9×10^{-5} S cm⁻¹ at 30 °C. The ionic conductivity can be further increased by mixing

Received:July 24, 2024Revised:September 30, 2024Accepted:September 30, 2024Published:October 9, 2024





Figure 1. Chemical structures of the synthesized orthoborate ionic materials containing $[P_{4444}]$ and $[N_{4444}]$ cations.

different OIPCs. For example, Abeysooriya et al.²⁸ showed that $[C_2epyr][FSI]$ and *N*-isopropyl-*N*-methylpyrrolidinium [FSI] ($[C_{(i3)}mpyr][FSI]$) OIPCs in a 1:9 molar ratio reached an ionic conductivity of 1.8×10^{-3} S cm⁻¹ at 30 °C. As unveiled by synchrotron XRD analysis, this mixture has increased defect volume and/or rotational disorder, which facilitates ion conduction.

Inspired by the work by Ue et al.,²⁹ focusing on bis(oxalato)borate anion ([BOB]) analogues with five-membered orthoborate rings, we aim to create OIPCs and have synthesized a series of new fluorine-free orthoborate-anion-based ionic materials using the bis(glycolato)borate ([BGB]) and bis(ethylene-1,2dioxy)borate anions ([BEDB]) combined with organic cations, such as tetrabutylphosphonium ([P₄₄₄₄]) and tetrabutylammonium ([N₄₄₄₄]) and compared with popular bis(oxalato)borate, [BOB]-based counterparts (Figure 1). However, as will be clear from below, not all our solid ionic materials are indeed (classical) OIPCs, and we will outline the underlying reasons. The structures and properties have been systematically investigated using various characterization techniques, with emphasis on the interactions present and with the final aim of verifying/dismissing their promise as battery electrolyte materials.

EXPERIMENTAL SECTION

Synthesis. The synthesis of orthoborate ionic materials was performed keeping in mind the 12 fundamental principles of green chemistry.³⁰ Briefly, the synthesis involved mixing of boric acid and the corresponding acid using water as the solvent to get the acidic form of the orthoborate, followed by a neutralization reaction with either tetrabutylphosphonium or tetrabutylammonium hydroxide.

[BEDB] Salts. Tetrabutylphosphonium bis(ethylene-1,2-dioxy)borate ($[P_{4444}][BEDB]$) and tetrabutylammonium bis(ethylene-1,2dioxy)borate ($[N_{4444}][BEDB]$) salts were prepared using a slightly modified procedure with respect to the previously reported synthesis path.³¹ Briefly, 0.02 mol ethylene glycol ($C_2H_6O_2$, Sigma-Aldrich, \geq 99%) and 0.01 mol boric acid (H_3BO_3 , Sigma-Aldrich, \geq 99.5%) were dissolved in 100 mL deionized water (H_2O , 18.25 M Ω cm, Millipore, Merck) and stirred at 60 °C for 3–4 h. Afterward, either 40 wt % tetrabutylphosphonium hydroxide aqueous solution (TCI, 40 wt %) or 40 wt % tetrabutylammonium hydroxide solution (Sigma-Aldrich, 40 wt %) was added to the reaction mixture followed by continuous stirring at 50 $^{\circ}$ C for 24 h. The water was removed at reduced pressure using a rotary evaporator to obtain the product. The product was washed with a mixture of ethyl acetate (VWR, technical) and hexane (VWR, technical) (1:1 volume ratio). Finally, the traces of solvents were removed using a rotary evaporator, and the product was dried in a vacuum oven at 90 $^{\circ}$ C for at least 2 days.

 $[P_{4444}][BEDB]$. White solid (95% yield). ¹H NMR (400.21 MHz, CDCl₃) δ 3.74 (s, 8H, -CH₂-O), 2.41–2.37 (m, 8H, -CH₂-P), 1.53 (s, 16H, -CH₂-), 0.99 (t, 12H, -CH₃) ppm. ¹³C NMR (100.64 MHz, CDCl₃) δ : 63.71, 24.28, 24.13, 24.06, 18.93, 18.46, 13.71 ppm. ¹¹B NMR (128.40 MHz, CDCl₃): 10.99 ppm. ³¹P NMR (162.01 MHz, CDCl₃): 33.10 ppm.

 $[N_{4444}][BEDB]$. White solid (89% yield). ¹H NMR (400.21 MHz, CDCl₃) δ 3.73 (s, 8H, -CH₂-O), 3.35-3.31 (m, 8H, -CH₂-N), 1.64-1-61 (m, 8H, -CH₂-) 1.49-1.40 (m, 8H), 1.01 (t, 12H, -CH₃) ppm. ¹³C NMR (100.64 MHz, CDCl₃) δ : 63.86, 58.70, 24.27, 19.91, 13.90 ppm. ¹¹B NMR (128.40 MHz, CDCl₃): 10.72 ppm.

[BGB] Salts. Tetrabutylphosphonium bis(glycolato)borate ([P4444]-[BGB]) and tetrabutylammonium bis(glycolato)borate ([N₄₄₄₄]-[BGB]) were prepared using the previously reported procedure. Briefly, 0.1 mol glycolic acid ($C_2H_4O_3$, Sigma-Aldrich, \geq 99%) and 0.05 mol boric acid were dissolved in 100 mL H₂O to form a homogeneous solution. The solution was stirred for 30 min at ambient temperature, followed by the addition of either 40 wt % tetrabutylphosphonium hydroxide solution or 40 wt % tetrabutylammonium hydroxide solution. The reaction mixture was continuously stirred at ambient temperature for 24 h, and then water was removed at reduced pressure using a rotary evaporator. The final product ([P4444][BGB]) was purified by washing with ethyl acetate and hexane (1:2 volume ratio). In the case of $[N_{4444}][BGB]$, a mixture of dichloromethane (VWR, technical) and hexane (1:1 volume ratio) was used to wash the product. Traces of solvents were rotary evaporated, and the final product was dried in a vacuum oven at 90 °C for 3 days.

 $[P_{4444}][BGB]$. White solid (98% yield). ¹H NMR (400.21 MHz, DMSO- d_6) δ 3.92 (s, 4H, -CH₂-O), 2.21-2.14 (m, 8H, -CH₂-P), 1.47-1.38 (m, 16H, -CH₂-), 0.92 (t, 12H, -CH₃) ppm. ¹³C NMR (100.64 MHz, DMSO- d_6) δ : 177.49, 65.55, 24.05, 23.90, 23.25, 23.21, 18.13, 17.66, 13.87 ppm. ¹¹B NMR (128.40 MHz, DMSO- d_6): 11.41 ppm. ³¹P NMR (162.01 MHz, DMSO- d_6): 33.80 ppm.

 $[N_{4444}][BGB]$. White solid (95% yield). ¹H NMR (400.21 MHz, DMSO- d_6) δ 3.92 (s, 4H, -CH₂-O), 3.18-3.14 (m, 8H, -CH₂-N), 1.56 (s, 8H, -CH₂-) 1.33-1.28 (m, 8H, -CH₂-), 0.93 (t, 12H, -CH₃) ppm. ¹³C NMR (100.64 MHz, DMSO- d_6) δ : 177.49, 65.55,

58.12, 23.67, 19.81, 14.08 ppm. ¹¹B NMR (128.40 MHz, DMSO-*d*₆): 11.41 ppm.

[BOB] Salts. Tetrabutylphosphonium bis(oxalato)borate ([P_{4444}]-[BOB]) and tetrabutylammonium bis(oxalato)borate ([N_{4444}][BOB]) were prepared using the previously reported procedure.²⁹ Briefly, 0.02 mol of oxalic acid ($C_2H_2O_4$, Sigma-Aldrich) and 0.01 mol of boric acid were dissolved in 100 mL of deionized H₂O to get a clear solution. The solution was stirred at 50 °C for 30 min, followed by addition of either 40 wt % tetrabutylphosphonium hydroxide solution or 40 wt % tetrabutylammonium hydroxide solution. The reaction mixture was stirred at 50 °C for 24 h, and water was removed using a rotary evaporator. The [P_{4444}][BOB] product was washed with ethyl acetate and hexane (1:1 volume ratio) at least 3 times. For [N_{4444}][BOB], a mixture of DCM and hexane (1:1 volume ratio) was used to purify the product. The final product was dried in a vacuum oven at 90 °C for 3 days.

 $[P_{4444}][BOB]$. Light yellow liquid (95% yield). ¹H NMR (400.21 MHz, DMSO- d_6) δ 2.22–2.15 (m, 8H, –CH₂–P), 1.48–1.40 (m, 16H, –CH₂–), 0.92 (t, 12H, –CH₃) ppm. ¹³C NMR (100.64 MHz, DMSO- d_6) δ : 158.75, 24.05, 23.90, 23.26, 23.22, 18.16, 17.68, 13.87 ppm. ¹¹B NMR (128.40 MHz, DMSO- d_6): 7.37 ppm. ³¹P NMR (162.01 MHz, DMSO- d_6): 33.78 ppm.

 $[N_{4444}][BOB]$. Light yellow liquid (85% yield). ¹H NMR (400.21 MHz, CDCl₃) δ 3.25–3.21 (m, 8H, –CH₂–N), 1.68–1.64 (m, 8H, –CH₂–), 1.46–1.40 (m, 8H, –CH₂–), 1.01 (t, 12H, –CH₃) ppm. ¹³C NMR (100.64 MHz, CDCl₃) δ : 158.97, 59.00, 23.99, 19.79, 13.67 ppm. ¹¹B NMR (128.40 MHz, CDCl₃): 7.66 ppm.

NMR Spectroscopy. Solution-state multinuclear (¹H, ¹³C, ¹¹B, and ³¹P) nuclear magnetic resonance (NMR) spectroscopy was performed using a Bruker Ascend Aeon WB 400 (Bruker BioSpin AG, Fällanden, Switzerland) spectrometer. The working frequencies were 400.21 MHz for ¹H, 162.01 MHz for ³¹P, 128.40 MHz for ¹¹B, and 100.64 MHz for ¹³C. Samples were dissolved in DMSO-*d*₆ or CDCl₃ and placed either in a 5 or 10 mm standard glass tube. All the solution (¹H, ¹³C, ¹¹B and ³¹P) NMR spectra are provided in Figures S1 and S21 in the Supporting Information (SI).

Solid-state multinuclear (13C, 11B, 31P, and 15N) magic-anglespinning (MAS) NMR experiments were carried out using the same spectrometer and either 5 mm (for ¹³C, ca. 100 mg samples) or 4 mm (for ¹¹B, ³¹P, and ¹⁵N, ca. 40 mg samples) MAS probes with samples (fine white powder) packed in zirconia rotors and spun at 5 or 8 kHz. The working frequencies for ¹³C, ¹¹B, and ³¹P were the same as above, and the working frequency for ¹⁵N NMR was 40.56 MHz. The NMR spectra were recorded using either the direct-excitation single-pulse experiment with proton decoupling or with cross-polarization (CP) from protons using ramping of the rf-field in the X-channel from 70 to 100% of the maximum amplitude and 2.5/2/1.5 ms contact time for ¹H-³¹P/¹H-¹³C/¹H-¹⁵N, respectively, and also with proton decoupling. A 93 kHz "Spinal-64" sequence³² for proton decoupling with rfpulses in the proton channel was used to average out the dipole-dipole $^{13}\text{C}^{-1}\text{H}/^{31}\text{P}^{-1}\text{H}/^{15}\text{N}^{-1}\text{H}$ interactions. ^{11}B and ^{31}P NMR spectra were externally referenced using liquid samples of $Et_2O \cdot BF_3$ (0 ppm) for ¹¹B and H_3PO_4 (85%, 0 ppm) for ³¹P. The liquid samples were placed in a small capillary (1 mm diameter) and inserted into an empty 4 mm rotor to minimize the differences in magnetic susceptibility between powder samples and the liquid reference. For ¹³C and ¹⁵N, solid adamantane (38.48 ppm from TMS, δ (¹³C) = 0 ppm) and polycrystalline ¹⁵Nenriched (98%) ¹⁵NH₄Cl (0 ppm) were used as external references. All measurements were performed at 293 K, and the NMR spectra were processed using Bruker Topspin 3.5 software. The solid-state (¹³C, ¹¹B, ³¹P and ¹⁵N) MAS NMR spectra are provided in Figures S22 and S33.

Thermal Characterization. Thermal gravimetric analysis (TGA) was carried out on a PerkinElmer TGA8000 instrument. About 3-5 mg of sample was placed in a ceramic crucible, and the experiment was performed from 30 to 600 °C at a heating rate of 10 °C min⁻¹. A PerkinElmer DSC6000 instrument was used for differential scanning calorimetry (DSC). For each experiment, ca. 2–4 mg of sample was sealed in an aluminum pan, and the experiment was performed under the N₂ gas atmosphere to exclude contact with the moisture or the air.

Specifically, DSC experiments were carried out from -80 to 200 °C at a heating rate of 5 °C min⁻¹. The intersection of the baseline and the tangent was determined using Pyris software to obtain the onset of the decomposition temperature ($T_{\rm decomp}$) and the glass transition temperature ($T_{\rm g}$). The melting points ($T_{\rm m}$) were obtained similarly from the DSC traces and also using an Electrothermal IA9000 Series Melting Point Apparatus, respectively.

The area under the DSC trace gives the enthalpy (ΔH) for a transition and is related to the change in entropy (ΔS) and the change in Gibbs free energy (ΔG) of a reaction according to the following (eq 1)

$$\Delta G = \Delta H - T \Delta S \tag{1}$$

Where *T* is the absolute temperature in Kelvin (K). When solid–solid transitions and solid–liquid (melting) phase transitions are reversible, ΔG in the equilibrium process equals to zero, and thus, ΔS of all these phase transitions can be expressed as the following eq (eq 2), which was used to analyze the molar entropies for the ionic materials

$$\Delta S = \frac{\Delta H \times M}{T} \tag{2}$$

Where *M* is the molecular weight (in $g \mod^{-1}$) of the bulk material.

FTIR Spectroscopy. A Bruker Tensor 27 FTIR spectrometer was used for FTIR spectroscopy. KBr pellets were made using a manual hydraulic press from Specac, UK. The FTIR spectra were recorded in the range from 400 to 4000 cm⁻¹ with 64 scans and with a resolution of 4 cm⁻¹.

lonic Conductivity. A Metrohm Autolab PGSTAT302N electrochemical workstation with an FRA32 M module was used for measurements of the ionic conductivity, and the data were processed using the Nova 2.1 software. A TSC 70 closed cell coupled to a temperature-controller Microcell HC (rhd Instruments, Germany) with ±0.1 °C accuracy was used for all liquid samples. The ionic conductivities were determined using electrochemical impedance spectroscopy (EIS) in the frequency range from 1 Hz to 1 MHz with an AC voltage amplitude of 10 mV_{rms} and a temperature range from -30 to 100 °C. A two-electrode setup was used for the assessment with a glassy carbon electrode (GC, diameter = 2 mm) and a 70 μ L Pt crucible as the counter electrode ($K_{cell} = 1.8736$ cm⁻¹). The cell was thermally equilibrated for 10 min before each experiment.

A TSC battery cell, coupled to a temperature-controller Microcell HC (rhd Instruments, Germany), with stainless steel disks as current collectors freshly polished by Kemet diamond paste (average particle size of ~250 nm) was employed for solid samples. In the case of solid samples with $T_{\rm m} < 100$ °C, a 0.2 mm spacer sandwiched between the two disc electrodes was used to control thickness of the film ($K_{\rm cell} = 0.039789 \text{ cm}^{-1}$). The powder sample was packed inside the cell and kept at 100 °C for 30 min to melt the sample, followed by cooling of the sample to ambient temperature, and the measurement was started after keeping the sample at ambient temperature for 1 h. For samples with $T_{\rm m} > 100$ °C, pellets with known thickness were made using a manual hydraulic press and the pellets were dried in a vacuum oven at 80 °C for 3 days prior to each experiment. The cell was thermally equilibrated for 20 min before each experiment.

Single-Crystal X-ray Diffraction. Single-crystal X-ray diffraction (SC-XRD) studies were carried out on $[P_{4444}][BGB]$ and $[N_{4444}][BGB]$ using crystals coated with NVH oil, mounted at the end of a cryoloop, and placed in the nitrogen cold stream (100 and 293 K) of an Xcalibur Eos diffractometer. The deviations of experimental temperatures are ± 2 K. Data were collected using MoK α radiation, and empirical absorption correction was carried out using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm (CrysAlisPro 1.171.42.89a; Rigaku Oxford Diffraction, 2023). The crystal structures were solved using SHELXT (intrinsic phasing) and refined using SHELXL-2018 (least-squares),^{33,34} with data processing carried out in Olex2.³⁵



Figure 2. TGA curves of (a) phosphonium-based and (b) ammonium-based orthoborate ionic materials.

RESULTS AND DISCUSSION

Here, we present a brief description of the thermal stability and phase behavior, followed by an assessment of the ionic conductivities of the orthoborate ionic materials. Next, the solid-state cation—anion interactions are systematically described with the help of FTIR and multinuclear (¹⁵N, ³¹P, ¹³C, and ¹¹B) solid-state NMR spectroscopy data, and finally, the crystal structures of two ionic materials at different temperatures are presented.

Thermal Properties. Thermal stabilities of the salts are significantly affected by the type of cation and the presence of carbonyl groups in the orthoborate anion (Figure 2). For a common anion, the salts with phosphonium cations exhibit higher thermal stabilities than those with ammonium cations, which agrees well with previous findings.³⁶ Overall, the T_{decomp} of the salts follows the sequence: $[P_{4444}][BGB] > [P_{4444}][BOB] > [P_{4444}][BEDB]$ and $[N_{4444}][BGB] > [N_{4444}][BOB] > [N_{4444}][BEDB]$. Thus, the salts with [BGB] anions are the most thermally stable, while the salts with [BEDB] and $[N_{4444}][BOB]$ and $[N_{4444}][BOB]$ revealed two-step decomposition paths; the first step with approximately 10% weight loss and the second with more than 80% weight loss. Among the six salts, $[P_{4444}][BGB]$ displayed the highest T_{decomp} value of about 400 °C.

The DSC traces reveal solid-solid phase transitions before melting (Figure 3). The DSC traces of [P₄₄₄₄][BEDB] and [P₄₄₄₄][BGB] indicate repeatable phase transitions in two consecutive cycles, while the salts with the $[N_{4444}]$ cation display slightly different thermal behavior in the second consecutive heating cycle. The peak #1 in these four solid ionic materials is the melting process, which is further confirmed by a melting point apparatus (Table S2). These ionic materials remain in plastic phases over different temperature ranges. Since the entropies of fusion (ΔS_{fus}) for these four salts are >20 J mol⁻¹ K^{-1} (Table S3) and they thus do not obey Timmermans' criterion,³⁷ not all of these ionic materials can be classified as plastic crystals.^{38,39} As the Timmermans' criterion was originally developed for simple molecular crystalline materials, but in our case, each material comprises cations and anions, making the system much more complex, e.g., only one ion might be involved in the rotational motions in the solid state, while the other exhibits rotational degrees of freedom only upon melting and, therefore, lead to a higher residual entropy of fusion. This has been observed for a series of ionic materials based on pyrrolidinium cations coupled to the bis(trifluoromethanesulfonyl) i/amide (TFSI/A) anion, exhibiting $\Delta S_{\rm fus}$ of 40–80 J mol⁻¹ K⁻¹.³⁸ Similarly, the dimethylammonium perrhenate plastic crystal displayed a $\Delta S_{\rm fus}$ of 38.2 J mol⁻¹ K⁻¹ attributed to the formation of a rotator phase before melting.³⁹

Both [P₄₄₄₄][BEDB] and [N₄₄₄₄][BEDB] exhibit relatively higher T_m, 158 and 169 °C, respectively (Table S2). [P₄₄₄₄]-[BEDB] displays a solid-solid phase transition at -59 °C, $\Delta S_{\text{II-I}}$ of which is larger than that of [N₄₄₄₄][BEDB] (25 vs 10 J mol⁻¹ K⁻¹), and remains in plastic phase I over a very wide temperature range from -59 to 158 °C (Table S3), which is much broader than for other reported OIPC materials.^{23,25} On the other hand, [N₄₄₄₄][BEDB] stays in phase I from 80 to 169 °C. The salts with the [BGB] anion have much lower T_m : 64 and 80 °C for [P₄₄₄₄][BGB] and [N₄₄₄₄][BGB], respectively (Table S2), and among the four ionic materials, $[P_{4444}][BGB]$ has the largest ΔS_{II-I} : 51 J mol⁻¹ K⁻¹ and [N₄₄₄₄][BGB] has ΔS_{II-I} of ca. 1 J mol⁻¹ K⁻¹. Unlike [N₄₄₄₄][BGB], remaining in phase I over a temperature range from 69 to 80 °C, [P₄₄₄₄][BGB] exhibits phase I over a larger temperature range from -6 to $64 \,^{\circ}$ C, which can be particularly beneficial for applications as a solid-state electrolyte. Unlike the other salts, the second cycle of [N₄₄₄₄][BGB] differs from the first one in terms of phase transitions and entropies (Table S4); there is an extra phase III evolved followed by a very narrow phase II in the range from 55 to 59 °C. Notably, ΔS_{fus} from the second cycle is much smaller compared to the first one: 23 vs $110 \text{ J mol}^{-1} \text{ K}^{-1}$.

The RTIL $[N_{4444}][BOB]$ exhibits glass transition temperature, $T_g = -33$ °C, while $[P_{4444}][BOB]$ exhibits a typical supercooled liquid behavior;⁴⁰ the glass transition/liquid–liquid transition at -58 °C is followed by a cold crystallization and subsequent melting (Figure 3e,f). A similar thermal phase behavior is observed for trihexyl(tetradecyl)phosphonium thiocyanate $[P_{666,14}][SCN]$ as well as trihexyl(tetradecyl)phosphonium borohydride $[P_{666,14}][BH_4]$ ILS.⁴⁰ The DSC data clearly show that the T_m decreases with an increase in the number of carbonyl groups of the anion, pointing to the importance of cation–anion interactions for the thermal stability, also important for the ion mobility and ionic conductivity.

lonic Conductivities. A comparison of the ionic conductivities of the RTILs and ionic materials is presented in Figure 4. For the RTILs, the ionic conductivity of $[P_{4444}][BOB]$ is higher than that of $[N_{4444}][BOB]$ over the whole studied temperature range, especially at lower temperatures. This agrees



Figure 3. DSC traces of (a) $[P_{4444}][BEDB]$, (b) $[N_{4444}][BEDB]$, (c) $[P_{4444}][BGB]$, (d) $[N_{4444}][BGB]$, (e) $[P_{4444}][BOB]$, and (f) $[N_{4444}][BOB]$.

well with the previously published data for RTILs with the 2-[2-(2-methoxyethoxy)ethoxy]acetate [MEEA] anion, [P₄₄₄₄]-[MEEA] and [N₄₄₄₄][MEEA], where the phosphonium RTIL exhibited a ~ 1.6-fold higher ionic conductivity (~0.1 vs ~ 0.06 mS cm⁻¹ at 20 °C).³⁶ The same is true for the ionic materials, as [P₄₄₄₄][BGB] has over one order-of-magnitude higher ionic conductivities than the molecularly analogous [N₄₄₄₄][BGB] salt (2.3×10^{-3} vs 1.0×10^{-4} mS cm⁻¹ at 20 °C).

Since $[P_{4444}][BGB]$ melts at 64 °C, the ionic conductivities of all of the orthoborate salts in this study are tabulated at 20 and 60 °C for a fair comparison between different ionic materials (Table S5). The ionic conductivities of $[P_{4444}][BGB]$ and $[N_{4444}]$ -

[BEDB] are comparable at both 20 and 60 °C. Among the solid ionic materials, $[N_{4444}][BGB]$ showed the lowest ionic conductivities throughout the whole studied temperature range, which is attributed to its lowest degree of disorder and strongest ionic interactions among systems in this study (see below). Consider that the method used for solid samples (with melting points of <100 °C), the change of ionic conductivity for $[N_{4444}][BGB]$ likely fits better to its DSC trace from the second cooling—heating cycle. On the other hand, the RTIL $[P_{4444}][BOB]$ displays the highest ionic conductivities, which might be due to its weak ionic interactions.



Figure 4. Ionic conductivities of organic orthoborate ionic materials. The data are taken from the first heating cycles.

Ionic Interactions, Structure, and Morphology. Ionic interactions were investigated using both FTIR and solid-state NMR spectroscopy, while structures were assessed by SC-XRD. FTIR spectroscopy is primarily employed to explore the cationanion interactions in these ionic materials, due to its excellent sensitivity toward coordination changes to the functional groups of the orthoborate anions. The FTIR spectra reflect the structural differences between the salts as, e.g., the C=Ostretching mode (1850–1650 $\mbox{cm}^{-1})$ of $[P_{4444}][BOB]$ and [N4444][BOB], which displays broad bands with multiple peaks around 1813 and 1780 cm⁻¹ with shoulders on both sides, while [P₄₄₄₄][BGB] and [N₄₄₄₄][BGB] show relatively sharp single peaks at 1737 cm⁻¹ (Figure 5). The [BGB] anion contains only one C=O group on each side of the boron atom, and the relative red shift implies stronger interactions within borate anions.^{41,42}

The solid-state multinuclear (^{15}N , ^{31}P , ^{13}C , and ^{11}B) NMR spectroscopy provides additional information about the



Figure 5. FTIR spectra of the orthoborate salts in the range from 2100 to 1000 cm^{-1} .

structure, dynamics, and cation-anion interactions in the ionic materials. The ¹⁵N CP-MAS NMR revealed that the nitrogen atom in the cation of $[N_{4444}][BGB]$, in which the anion [BGB] has two carbonyl groups, is additionally deshielded by ca. 3 ppm as compared to the nitrogen atom in $[N_{4444}][BEDB]$, in which the anion [BEDB] has no carbonyl groups in its structure (Figure 6a). This further supports that the polar carbonyl groups, which are electron-withdrawing by inductive effects, play a key role in the ionic interactions⁴³ and is further confirmed by the ³¹P CP-MAS NMR spectra of the phosphonium-based salts (Figure 6b). Again, the ³¹P NMR resonance line of [P₄₄₄₄][BGB] is observed at a higher chemical shift compared to its structural analogue without any carbonyl groups, i.e., [P4444][BEDB]. However, the additional deshielding of the P atoms in the former salt is considerably smaller (ca. 0.5 ppm for 31 P vs ca. 3 ppm for 15 N), that despite higher sensitivity of isotropic chemical shifts of ¹⁵N to the structural changes, they still point to weaker cation-anion interactions in $[P_{4444}][BGB]$ as compared to $[N_{4444}][BGB]$.

The ¹³C CP-MAS NMR spectra revealed resonance lines in the range from 172 to 180 ppm and 60 to 72 ppm, which are assigned to carbon sites in C=O and [-C(O)-] groups of anions [BEDB] and [BGB] in ionic materials, respectively (Figure 6c). The phosphonium-based salts display single resonance lines for C=O and [-C(O)-] groups, while pairs of resonance lines for these carbon sites are observed for the ammonium-based salts. This clearly indicates that the carbon atoms are chemically inequivalent in the latter, either in the same anion or in two anions having different conformations in the asymmetric unit, as in bis(salicylato)borate salts reported previously.⁴⁴ Additional broadening and characteristic "molecular-motion-distorted" line shapes of resonance lines in the spectrum of [P4444][BGB] could be due to conformational and rotational dynamics of anions in this ionic material at the ambient temperature of the ¹³C CP-MAS NMR experiment (293 K), which is correlated with the ionic conductivity data (an abrupt change in conductivity from ca 10^{-8} to 10^{-6} S cm⁻¹) nearby this temperature (see blue triangles in Figure 4).

¹¹B single-pulse MAS NMR spectra of these ionic materials display a single resonance line for the boron atom in anions for all salts in this study (Figure 6d). Although the chemical shifts are very similar, the ¹¹B resonance lines of the ammonium-based salts are significantly broader (Table S6), suggesting either larger structural distortions in the BO₄ moiety (¹¹B is a quadrupolar nucleus with spin I = 3/2) or the presence of orthoborate anions with different conformations in these ammonium salts.⁴⁵

In view of the fact that $[P_{4444}][BGB]$ and $[N_{4444}][BGB]$ crystallize well, we characterized these salts in the solid state by SC-XRD to get deeper insights into their structure (Figure 7). The $[N_{4444}][BGB]$ crystallizes in the triclinic space-group P1, whereas the [P₄₄₄₄][BGB] crystallizes in the monoclinic spacegroup C2/c. In each case, a borate ion forms a spirocyclic motif, with the central boron atom coordinated by two chelating glycolate ions, each bound through an alcoholate group and a carboxylate group. Notable structural features within the borate ions are that the $B-O_{alcoholate}$ bonds are shorter (O6–B1, O3– B1 = 1.414(5) - 1.449(2) Å) than the $B - O_{carboxylate}$ bonds (O4-B1, O1-B1 = 1.497(6) - 1.515(5) Å) (Figures S34-S35 and Tables S7–S11). Moreover, in the five-membered chelate rings, the glycolate carboxylate carbons distort away from an idealized trigonal planar geometry (all bond angles at 120°), resulting in smaller C-C-O_{carboxylate-B} angles (C4-C3-O4, C2-C1-O1 = $108.9(1)-109.0(1)^{\circ}$). These angles approach the bond angle



Figure 6. Solid-state NMR spectra of the ionic materials: (a) ¹⁵N CP-MAS, (b) ³¹P CP-MAS, (c) ¹³C CP-MAS (parts of the spectra corresponding to anions), and (d) ¹¹B single-pulse MAS NMR spectra. The MAS frequencies were 5 kHz in Figure 6a, 6b, and 6d and 8 kHz in Figure 6c. The numbers of signal transients were 77 238 and 84 084 from top to bottom in Figure 6a, 4 in Figure 6b, 1358, 1358, 3978, and 3978 from top to bottom in Figure 6c, and (d) 64 in Figure 6d.

expected for a regular pentagon (108°) , showing how the glycolate ion distorts when it becomes part of a chelate ring with boron.

Furthermore, when inspecting the C-C-C-C torsion angles of the butyl groups, it can be seen that all butyls in [N₄₄₄₄][BGB] assume a zigzag conformation (176.8(1)–179.2(1)°). Similarly, three of the butyl groups in [P₄₄₄₄][BGB] assume a zigzag conformation $(171.4(4)-179.4(4)^{\circ})$, whereas the fourth assumes a coiled conformation (torsion angle $69.9(5)^{\circ}$). The [BGB] ions have one C=O group showing three contacts and another C=O group showing one contact to the cations. This is both the case for the $\left[P_{4444}\right]$ and for the $\left[N_{4444}\right]$ salt. It is, however, notable that the contacts involve two $\left[\mathrm{P}_{4444} \right]$ cations in $[P_{4444}][BGB]$ but three $[N_{4444}]$ cations in $[N_{4444}][BGB]$ (Figure S35 and Table S12). These structural features could be correlated with the solid-state NMR data, where the [N4444] cation affects the [BGB] anion by giving rise to two ¹³C resonance lines for the carbon atoms and the broadness of the ¹¹B resonance line. Thus, despite their chemically similar composition, [N₄₄₄₄][BGB] and [P₄₄₄₄][BGB] pack in entirely different ways, in line with their disparate physical properties.

For $[N_{4444}][BGB]$, the crystal packing is defined by space group $P\overline{1}$ at both 100 and 293 K (corresponding to Phase II), and the packing is essentially isostructural at these temperatures (Figure S36). At the higher temperature, the thermal ellipsoids become larger, and the cell distances, *a* and *b*, increase significantly, from 9.5669(3) to 9.7009(6) Å and 10.9146(3) to 11.0731(6) Å. On the other hand, *c* only increases from 12.4087(4) to 12.4567(7) Å. At the same time, the cell angle, γ , increases from 64.783(3)° to 65.628(5)°, whereas α and β are almost unchanged.

In contrast, for [P₄₄₄₄][BGB], the crystal packing changes from space group C2/c at 100 K (Phase II) to $P\overline{1}$ at 293 K (Phase I, two crystallographically independent formula units per unit cell in the triclinic case). The close similarity in crystal packing for [P₄₄₄₄][BGB] can be seen by viewing the triclinic and monoclinic crystal structures along the crystallographic c-axes, which gives a reasonably good overlay (Figure 8). The roomtemperature structure shows large thermal ellipsoids, and the disorder in several of the butyl chains of the cations is noticeable. It is also noticeable that whereas the unit cell volume increases only slightly when [N₄₄₄₄][BGB] goes from 100 to 293 K $(1117.99(7) \text{ Å}^3 \text{ to } 1162.55(13) \text{ Å}^3)$, the unit cell volume for $[P_{4444}][BGB]$ goes from 4660.7(5) Å³ (monoclinic) to 2530.86(16) $Å^3$ (triclinic) when the temperature increases, i.e., a volume expansion of 8.6% per formula unit of [P₄₄₄₄][BGB]. Although no visible phase transitions are detected in the DSC curves upon heating from 10 to 50 °C, there exists an obvious increase in the ionic conductivity of [P₄₄₄₄][BGB] from 10 to 20 °C, which agrees well with the structural changes.

CONCLUSIONS

The presence of electron-withdrawing carbonyl groups in the orthoborate anions plays a key role in their ionic interactions as well as structures and fundamental properties. The salts totally







Figure 8. Change of the crystal packing for [P₄₄₄₄][BGB] from monoclinic at 100 K to triclinic at 293 K.

without and with two carbonyl groups in their anions, i.e., the [BEDB] and [BGB], exhibit plastic crystal behavior, while the [BOB]-based salts containing four carbonyl groups remain liquid at ambient temperature. The [BGB] anion-based salts revealed superior thermal stability, and their structures are significantly affected by the countercation, as confirmed by FTIR, X-ray crystallographic studies, and multinuclear solid-state NMR spectroscopy. This work sheds light on the structure–property relationship of orthoborate-based ionic materials and will facilitate the structural designability of

fluorine-free organic ionic plastic crystals for energy storage applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.4c01030.

Solution sate (¹H, ¹³C, ¹¹B, and ³¹P) NMR spectra; solidstate (¹³C, ¹¹B, ³¹P, and ¹⁵N) MAS NMR spectra; decomposition and phase transition temperatures; comparison of ionic conductivity; line widths of resonance lines for solid-state ¹¹B MAS NMR spectra; X-ray crystallographic studies (PDF)

Accession Codes

CCDC 2337095–2337096 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Swedish Research Council for Sustainable Development (Grant number: 2020-00969), and P.J. is also grateful for the financial support from his Swedish Research Council (VR) Distinguished Professor grant "Next Generation Batteries" (#2021-00613). The Foundation in memory of J.C. and Seth M. Kempe (project numbers JCK-1306 and JCK-1433) and the laboratory found at LTU are acknowledged for providing grants, from which a Bruker Aeon/Avance III NMR spectrometer at LTU has been purchased.

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