Lithium and Sodium Benzimidazolate Coordination Networks: Syntheses, Structures and Thermal Properties

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Abstract

Alkali metal imidazolates are important compounds, serving as intermediates in organic synthesis and additives in alkali ion electrolytes. However, their solidstate structures and thermal behaviors



remain largely unexplored. In this study, we present the synthesis, structural analysis and thermal characterization of lithium and sodium benzimidazolate (bim⁻). The crystal structures of these microcrystalline materials, determined by 3D-electron diffraction, reveal closely related layered coordination networks. In these structures, fourfold *N*-coordinated alkali ions are bridged in two dimensions by bim⁻ linkers, with the networks' surfaces decorated by the phenyl rings of the bim⁻ linkers, stacking atop one another in the solid state. Differential scanning calorimetry combined with variable temperature X-ray powder diffraction indicate that both materials melt above 450 °C. Additionally, Na(bim) undergoes a displacive phase transition from an ordered α -phase to a highly disordered β -phase before melting. Structural variations, primarily attributable to the differing ionic radii of Li⁺ and Na⁺, result in distinct coordination environments of the alkali metal ions and varying orientations of the bim⁻ linkers. These differences lead to markedly distinct thermal behaviors: Li(bim) exhibits positive thermal expansion along all crystal axes, whereas Na(bim) switches from area negative thermal expansion (NTE) to linear NTE during the $\alpha \rightarrow \beta$ phase transition.

Introduction

Metal imidazolates form the basis for several different functional materials. The most prominent example is the family of zeolitic imidazolate frameworks (ZIFs), a subgroup of metal-organic frameworks (MOFs), exhibiting zeolitic topologies with open pores.^{1,2} ZIFs consist of divalent transition metal ions, such as Zn²⁺ and Co²⁺, which are tetrahedrally coordinated by the nitrogen atoms from imidazolate-type linkers that bridge adjacent metal centers. The imidazolates' structure-directing effect arises from the close resemblance of the metal-imidazolate-metal bond angle (around 145°) to the Si–O–Si bond angle observed in silicates and zeolites.³ ZIFs are often subject to studies focusing on gas physisorption and separation applications due to their porous nature combined with a rather high chemical and thermal stability inherent to some members of this class of materials.^{4,5} In the last decade many ZIF structures have been reported including mixed linker and mixed metal ZIFs⁶⁻⁸ that feature different metal ions, such as Fe^{2+,9} Cd^{2+,10,11} Mn^{2+,12} and Mg^{2+,13} By formal substitution of half of the divalent metal ions by trivalent B³⁺ and the other half by monovalent metal ions, such as Cu⁺ or Li⁺, a related class of materials denoted as boron imidazolate frameworks (BIFs) can be obtained.^{14,15} While some BIFs exhibit zeolitic topologies, others such as BIF-40 (chemical composition: $CuBH(bim)_3$, $bim^- = benzimidazolate$) feature coordination units with trigonal connectivity and exhibit reductive properties originating from the hydridic hydrogen atom of [BH(bim)₃]^{-.15,16}

In addition to the highly porous crystalline structures of ZIFs, their thermal properties have recently attracted significant interest.¹⁷ Studies have shown that certain ZIFs, specifically those based on Zn²⁺, Co²⁺, and Fe²⁺, can melt when heated to temperatures between around 400 °C to 600 °C under an inert atmosphere.^{18–21} Upon cooling, these melts form amorphous glasses that retain some of their microporosity,^{22,23} making them valuable for applications such as gas separation membranes^{24,25} and (quasi-)solid electrolytes.^{26,27} This melting and glass-forming ability is particularly noteworthy as it allows the materials to be shaped and molded in their liquid state, a capability not available in conventional non-meltable MOFs or coordination networks.^{28,29} This unique property expands the practical applications and processing possibilities of ZIF-based materials, offering new opportunities for innovation in various fields.

Compared to the extensive structural information available for divalent metal imidazolates (e.g., ZIFs) and BIFs, very little is known about the solid-state structures

of the simplest alkali imidazolate salts. This is surprising given the chemical simplicity of such compounds and their role in chemical synthesis and as additives for liquid lithium ion electrolytes. Examples from chemical synthesis include the preparation of *N*-functionalized imidazoles or the synthesis of imidazolium-based ionic liquids,^{30–32} while several derivatives of lithium 4,5-dicyanoimidazolate salts are highly potent additives for liquid lithium ion electrolytes.^{33–35} Given the demand for such alkali imidazolate salts is high, advanced knowledge about their synthesis, solid-state structures and thermal properties is crucial for their application. Due to their high hydrophilicity and the challenges associated with growing larger single crystals, only a very small number of alkali imidazolates have been structurally characterized to date. These include some alkali imidazolate salts A(im) (im⁻ = imidazolates.^{36–38} A notable example is a microporous high-temperature polymorph of Na(im), which is obtained by heating the dense room temperature polymorph of Na(im) to 212 °C under an inert atmosphere.³⁸

In this work, we report the synthesis, structural analysis and thermal characterization of lithium and sodium benzimidazolate, Li(bim) and Na(bim). The crystal structures of the microcrystalline materials were derived from 3D electron diffraction (3DED) and variable temperature (VT) X-ray powder diffraction (XRPD). Both materials form 2D coordination networks with closely related structures. Differential scanning calorimetry (DSC) reveals that both materials melt at temperatures beyond 450 °C and fully recrystallize upon cooling the liquid phases. DSC and VTXRPD uncover that Na(bim) undergoes a thermally induced phase transition from a room temperature α -phase to a high-temperature β -phase before melting. The displacive phase transition can be explained by a highly anisotropic thermal expansion behavior of the α -phase which displays the very rare phenomenon of area negative thermal expansion behavior of Na(bim) originates from lattice vibrations and dynamical disorder in the crystal structure.

Results and Discussion

Synthesis and Structural Characterization

Li(bim) and Na(bim) were synthesized via an acid-base reaction of benzimidazole (*n*-BuLi) (Hbim) dissolved in dry THF with *n*-butyllithium or sodium hexamethyldisilazide (NaHMDS) as the metalation agents (see Experimental Section). While Li(bim) precipitates directly from the reaction solution, precipitation of Na(bim) was initiated by the addition of *n*-hexane to the reaction mixture. After washing the obtained powders with *n*-hexane, solvent residues and unreacted Hbim were removed by heating the products at 280 °C under a dynamic vacuum. Li(bim) was obtained as a colorless and Na(bim) as a slightly yellow but strongly hygroscopic microcrystalline powder. ¹H NMR spectra of the alkali salts dissolved in DMSO-*d*₆ and DCI/D₂O display only signals assigned to the hydrolysis product benzimidazole (Figures S1 and S2). The absence of HMDS byproducts in Na(bim) was proven by ²⁹Si NMR measurements (Figure S3). The absence of N–H stretching vibrations in the range from 2500 cm⁻¹ to 3200 cm⁻¹ in Fourier transform infrared (FTIR) spectra of the reaction products additionally proves the full deprotonation of Hbim (Figure S12). To further verify the chemical identity of the reaction product, thermal decomposition of the alkali salts under air was studied with simultaneous thermogravimetric and differential thermal analysis (STA), resulting in a total mass loss of 90.0% for Li(bim) (calc.: 90.6% for complete combustion to Li₂O) and 78.8% for Na(bim) (calc.: 78.0% for complete combustion to Na₂O) in the temperature range from 50 °C up to 1200 °C (see Figures S6 and S7).

The crystal structures of Li(bim) and α -Na(bim) (i.e. the room temperature phase of Na(bim); the high temperature β -phase is discussed below) were solved by 3DED from submicron-sized crystals (Figure 1 and S8). Both materials crystallize in the orthorhombic crystal system in the space groups *Cmme* (Li(bim)) and *Pbcm* (α -Na(bim)). In both cases, the alkali ions are fourfold coordinated by the N atoms of four bim⁻ linkers. The [LiN₄] polyhedra in Li(bim) exhibit a flattened tetrahedral coordination geometry with a geometry index $\tau_4 = 0.68$ (with $\tau_4 = 1$ for the perfect tetrahedral environment and $\tau_4 = 0$ for the perfect square planar environment)³⁹, whereas the [NaN₄] polyhedra in α -Na(bim) feature an unusual coordination environment that is close to a square planar configuration ($\tau_4 = 0.23$). In both structures, each N atom of the bim⁻ linkers bridges between two adjacent Li⁺ or Na⁺ ions so that each linker has contact to four alkali ions. The [LiN₄] and [NaN₄] polyhedra are connected with

neighboring polyhedra by edge-sharing forming 1D inorganic rods that are bridged in the second dimension by bim⁻ linkers to generate layered coordination networks. The phenyl rings of the bim⁻ linkers are oriented alternatingly on opposite sides of the layer plane. The alkali ions as well as the bim⁻ units can both be regarded as four connecting vertices, so that the network topology can be classified as a binary square lattice (**sql**). In Li(bim), the bim⁻ linkers are arranged perfectly perpendicular to the layer plane, whereas in Na(bim) they alternatingly tilt away from the plane normal, leading to a herringbone-like pattern when viewed along the crystallographic *c*-axis.

The 2D coordination networks are tightly stacked on top of each other in the third dimension forming a layered van-der-Waals crystal. The layer-layer distance (*c*-axis of Li(bim) and *a*-axis of α -Na(bim)) is much shorter for α -Na(bim) ($a_{3DED} = 8.7500(17)$ Å) than for Li(bim) ($c_{3DED} = 11.921(2)$ Å). This is because neighboring layers feature a stronger interdigitation of the bim⁻ linkers in α -Na(bim) because of their alternate tilting.



Figure 1. Crystal structures of Li(bim) and α -Na(bim) with Li (yellow), Na (pink), C (brown), N (blue). Hydrogen atoms are omitted for clarity. a, c) Perspective view on the coordination environments of the metal sites in Li(bim) and α -Na(blm) with displacement ellipsoids drawn at the 50% probability level. b, d) Orthographic representations of supercells of the crystal structures of Li(bim) and α -Na(bim) viewed along the crystallographic main axes.

The phase purity of the bulk materials was proven by structureless profile fits (Pawley method⁴⁰) to XRPD patterns recorded at room temperature (see Figure S13 and S14). The lattice parameters obtained from the profile fit (Table S4) are 3% to 6% smaller than those derived from 3DED (Table S1), resulting in significantly smaller unit

cell volumes from XRPD data. Specifically, the unit cell volume of Li(bim) from XRPD is 11.6% smaller, and that of Na(bim) is 13.7% smaller, compared to 3DED. This discrepancy can be attributed to the lower accuracy of the unit cell parameters provided by 3DED, due to various experimental challenges associated with the method and instrument.⁴¹

We note that a synthesis protocol for Li(bim) and some basic structural characterization, including unit cell parameters and space group symmetry, were recently reported in a doctoral thesis.³⁷ However, atomic coordinates were not provided. The thesis proposed the space group symmetry *Pmca*, which is a non-isomorphic subgroup (albeit in a different axis setting) of the space group *Cmme* derived via 3DED.³⁷ We confirmed the validity of the structure with space group *Cmme* by profile fitting of the XRPD data of Li(bim), which showed that none of the additional Bragg reflections of the subgroup *Pmca* have non-zero intensity in the XRPD pattern (Figure S16).

Thermal Phase Behavior

STA of Li(bim) and Na(bim) in open alumina crucibles under an inert N₂ flow revealed that the materials thermally decompose at 406 °C and 384 °C, respectively (Figure S4 and S5). In contrast, DSC analyses up to a temperature of 500 °C in hermetically sealed aluminium crucibles (Figure 2a) display endothermic melting signals at 487 °C with a melting enthalpy (ΔH_m) of 26.9 kJ mol⁻¹ for Li(bim) and at 453 °C with a ΔH_m of 24.7 kJ mol⁻¹ for Na(bim). The assignment of the endothermic signals to melting events is based on the loss of Bragg reflections in variable temperature (VT)XRPD patterns collected at 500 °C (Figure 2b; samples sealed in quartz capillaries) and the transformation of a loose microcrystalline powder to monolithic shapes of sintered particles after heating the materials across their melting point in the DSC apparatus (see Figure S11). The slightly higher T_m and ΔH_m of Li(bim) compared to Na(bim) can be explained by the higher charge density of the smaller Li⁺ ion compared to Na⁺, leading to stronger ionic bonds for Li(bim). The observation that the materials only melt when heated in sealed vessels suggests they have a high vapor pressure below their melting temperatures. Consequently, if the samples are in an open environment, they decompose rather than melt, while they have a higher thermal stability and form a liquid if they are in a closed vessel.

Na(bim) shows an additional weaker endothermic signal in the DSC upscan at 166 °C. This signal corresponds to a first-order solid-solid phase transformation from the room-temperature α -phase to a high-temperature β -phase. Determination and refinement of the crystal structure of the β -phase of Na(bim) from the VTXRPD data was successful and is discussed below. Li(bim) shows no additional phase change besides the melting event in the temperature range studied.

Cyclic DSC experiments, consisting of two consecutive heating-cooling cycles, prove that all phase transitions are reversible (Figure S8 and S9). While cooling the liquid Na(bim) from 470 °C to 100 °C, the exothermic recrystallization of the material occurs at 412 °C followed by the exothermic $\beta \rightarrow \alpha$ transition at 157 °C. The absolute value of the corresponding phase change enthalpies of Na(bim) is very close to those of the heating branch, thus indicating that thermal decomposition of the liquid Na(bim) at high temperatures is negligible. In contrast, the absolute value of the melting and recrystallization enthalpies of Li(bim) decreases during thermal cycling between 100 °C and 500 °C, suggesting partial thermal decomposition of the material at high temperature.



Figure 2. a) Heat flow curves of DSC data of Li(bim) and Na(bim) in a DSC experiment with a constant heating rate of 10 °C min⁻¹ from room temperature up to 500 °C. b) *In-situ* VTXRPD patterns of Li(bim) and Na(bim) (λ = 0.1616 Å) monitoring the thermal expansion and the phase transition from α - to β -Na(bim). The XRPD pattern recorded at 500 °C feature only diffuse scattering in agreement with the melting signal in the DSC data.

The sharp peak observed in the heat flow curve of the DSC data during the $\alpha \rightarrow \beta$ phase transition of Na(bim) suggests that the transition is of a displacive nature, while the rather low $\Delta H_{\alpha \rightarrow \beta}$ (1.3 kJ mol⁻¹) and $\Delta S_{\alpha \rightarrow \beta}$ (2.9 J K⁻¹ mol⁻¹) indicate that the transition does not involve a major rearrangement of the structure.⁴² The XRPD pattern of the β -phase has fewer reflections than the pattern of the α -phase, implying that β -Na(bim) has a higher symmetry (see Figure 2). Indeed, the diffraction pattern of β -Na(bim) can be indexed with a slightly expanded unit cell in the space group *Aemm*, a minimal non-isomorphic supergroup of space group *Pbcm* (the symmetry of α -Na(bim)).⁴³ For structureless profile fitting (Pawley method⁴⁰), the non-standard space

group setting *Aemm* was transformed to the conventional setting *Cmme* by axis transformation (see Supplementary Information for details), yielding an excellent fit to the experimental XRPD pattern recorded at 200 °C. All other minimal non-isomorphic subgroups of *Pbcm* failed to provide a good fit to the data.



Figure 3. Crystal structure of β -Na(bim) with Na (pink), C (brown) and N (blue). Hydrogen atoms are omitted for clarity. a) Coordination environment of Na atoms without positional disorder (i.e. only the atoms of one half-occupied molecular fragment are shown). The atomic radii correspond to the atoms' isotropic displacement parameters (drawn at a 50% probability level). b) View on the coordination environment of Na atoms featuring positional disorder. The two Na(bim) molecular fragments (full-colored and color-desaturated) are translated along the *c*-axis and have an atomic occupancy of $\frac{1}{2}$ each. c, d, e) Orthographic views of supercells of a simplified ordered structure of β -Na(bim) obtained by averaging the atomic positions of the two molecular fragments shown in panel b. Views along the crystallographic main axes are shown.

An initial structural model for β -Na(bim) was generated from the structure of α -Na(bim) through axis transformation and enforcement of *Cmme* symmetry (Figure 3). Subsequent Rietveld refinement⁴⁴ against the VTXRPD data of Na(bim) recorded at 200 °C resulted in a highly disordered structural model providing a good fit to the experimental data with satisfactory reliability factors ($R_{wp} = 1.49\%$, $R_{exp} = 1.80\%$, $R_{Bragg} = 0.95\%$; details in the Supplementary Information). The derived structure of β -Na(bim) closely resembles that of Li(bim), which is also crystallizing in *Cmme*. The model for β -

Na(bim) depicts a structure where the bim⁻ linkers are oriented perfectly perpendicular to the coordination network layers. The refined isotropic atomic displacement parameters (ADPs) of the C and N atoms of the bim⁻ linker indicate that these units strongly oscillate about the direction of the crystallographic a-axis (Figure 3a). Additionally, a dynamic displacement of all network atoms orthogonal to the plane of the 2D coordination network was evident in the Fourier difference map. Modeling this transverse displacement using anisotropic ADPs was not feasible due to the limited number of observed reflections in the XRPD data, resulting from the relatively poor scattering power of β-Na(bim) at 200 °C. Consequently, the displacement was accounted for by a split model representing two sets of atoms, each with 50% occupancy, displaced along the c-axis (Figure 3b). The large dynamic displacement of the atoms perpendicular to the plane of the 2D network is already apparent in the anisotropic ADPs of the Na, N and C atoms in the structural model of α -Na(bim) derived by 3DED (Figure 1c). Therefore, it is proposed that large amplitude transverse lattice vibrations drive the phase transition from the α - to the β -phase in Na(bim). Remarkably, the coordination environment of the Na⁺ ions markedly changes from close to squareplanar in α -Na(bim) (τ_4 = 0.23) to a more tetrahedral environment in β -Na(bim) (τ_4 = 0.45)39.

Structureless profile fitting of the VTXRPD patterns of Li(bim) and Na(bim) (Figure 2b) in the temperature range from 30 °C to 400 °C provided comprehensive information on the thermal expansion of the coordination networks and gave more insights into the $\alpha \rightarrow \beta$ phase transition of Na(bim) (Figure S18 and S20). To aid the comparison of the different phases involved, we define a set of orthogonal principal axes *X*, *Y* and *Z* (Figure 4a), which correspond to the lattice vectors lying parallel to the layer of the coordination networks (i.e. *X* along the rods of edge-connected [LiN₄]/[NaN₄] polyhedra and *Y* along the bridging direction of the bim⁻ linkers) and the lattice vector perpendicular to it (*Z*). The relationship between the crystallographic lattice vectors *a*, *b*, *c* and the principal axes is given in Table S6. The corresponding linear thermal expansion coefficients α_l (l = X, *Y*, *Z*) describe the temperature-dependent change of the length of the principal axes *l* at constant pressure $(\alpha_l = \frac{1}{l} \frac{dl}{dT})$, whereas the volumetric thermal expansion coefficient $\alpha_V = \frac{1}{V} \frac{dV}{dT}$) (see Section S7.2 in the SI for details).

The thermal expansion coefficients are in the order of 10^{-6} K⁻¹ and are given in the unit MK⁻¹ (1 MK⁻¹ = 10^{-6} K⁻¹).



Figure 4. a) Definition of the principal axes of expansion *X*, *Y* and *Z* illustrated with a generic A(bim) crystal structure with the metal ion A⁺ = Li⁺, Na⁺ (violet), N (blue), and C (brown). b,c) Progression of the principal axes *X*, *Y* and *Z* and the unit cell volume *V* of Li(bim) (b) and Na(bim) (c) in the temperature range from 30 °C to 400 °C. Na(bim) exhibits the $\alpha \rightarrow \beta$ phase transition at $T_{\alpha \rightarrow \beta}$ = 166 °C. The lines are linear fits to the data. The uncertainties of the data are smaller than the size of the symbols. The graphical insets show excerpts of the crystal structures of the corresponding phases present in the respective temperature ranges with Li (yellow), Na (pink), C (brown), N (blue). Hydrogen atoms are omitted for clarity.

Li(bim) continuously expands along all principal axes with the largest coefficient of thermal expansion (α) along the principal axis *X* ($\alpha_X = 92(5)$ MK⁻¹), which is the direction along the [LiN₄] polyhedral rods (Figure 4b, Table 1). Along the principal axis *Y* (direction of bim⁻ linkers bridging between the polyhedral rods) and the principal axis *Z* (stacking direction of the 2D network), the thermal expansion is substantially smaller ($\alpha_Y = 40.0(6)$ MK⁻¹, $\alpha_Z = 22.3(10)$ MK⁻¹), resulting in a volumetric thermal expansion coefficient α_V of 154(5) MK⁻¹ and a total expansion by about 6% during heating from 30 °C to 400 °C (see Section S7.2 in the SI for details).

The thermal expansion behavior of Na(bim) differs substantially from the one of Li(bim) (Figure 4c, Table 1). Up to the $\alpha \rightarrow \beta$ phase transition at approximately 166 °C, α -Na(bim) shows a very large volumetric thermal expansion coefficient α_V of about 304 MK⁻¹. The strong volumetric expansivity originates from the drastic expansion of the material along the Z axis ($\alpha_Z \approx 343 \text{ MK}^{-1}$), whereas X and Y both contract upon heating ($\alpha_X \approx -26$ MK⁻¹, $\alpha_Y \approx -13$ MK⁻¹). Thus, α -Na(bim) displays the very rare phenomenon of area negative thermal expansion (NTE)⁴⁵ with an area expansivity α_A = α_X + $\alpha_Y \approx -39$ MK⁻¹. The magnitude of α_A of α -Na(bim) is substantially larger than those of other materials featuring this property, for example LiBeBO₃ ($\alpha_A = -5.07(21)$) MK⁻¹)⁴⁶ and Zn(isonicotinate)₂ ($\alpha_A = -21.8(10)$ MK⁻¹)⁴⁵. The area NTE of α -Na(bim) acts in the layer of the 2D networks and can be explained by the large amplitude vibrations transverse to the layer plane (i.e. parallel to Z). These vibrations are also responsible for the $\alpha \rightarrow \beta$ phase transition (Figure 1c and 3b). In accordance with this rationale, the principal axes X and Y further contract by 1.7% and 0.5%, respectively, during the $\alpha \rightarrow \beta$ phase transition, while Z expands by 7.5%, resulting in a volume increase of 5.9%. The large expansion of Z is driven by the vibrational motion of the network's building units in β -Na(bim) and the change in the geometry of the [NaN₄] polyhedra from close to square planar (α -phase) to more tetrahedral (β -phase) as discussed above. Upon further heating, β -Na(bim) keeps expanding primarily along the Z axis, even though α_Z (183.7(4) MK⁻¹) is only about half as large as for α -Na(bim). Moreover, α_X is positive (54(5) MK⁻¹) and α_Y remains negative (-18.5(17) MK⁻¹) in β -Na(bim), so that the material switches from area NTE to linear NTE at the $\alpha \rightarrow \beta$ phase transition. The volumetric expansivity is smaller in β -Na(bim) compared to α -Na(bim) but α_V is still larger than the one of Li(bim) and amounts to 219(6) MK⁻¹. This again is a signature of the large amplitude lattice vibrations of β -Na(bim) and the weaker metal-

nitrogen bonds in Na(bim) compared to Li(bim), consistent with the lower melting temperature of the sodium derivative.

Table 1. Linear and volumetric thermal expansion coefficients of Li(bim), α - and β -Na(bim). The principal axes *X*, *Y*, and *Z* correspond to the crystallographic axes *a*, *b*, and *c* for Li(bim) and β -Na(bim), and to *b*, *c*, and *a* for α -Na(bim). Standard deviations for the thermal expansion coefficients of α -Na(bim) are not provided, as only two datasets have been recorded for this phase. Overall, the reliability of the reported uncertainties is constrained by the limited number of diffraction patterns recorded at varying temperatures (see Table S7 and S8)."

	α_X / MK ⁻¹	$\alpha_{\rm Y}/{\rm MK^{-1}}$	α_Z / MK^{-1}	α_V / MK ⁻¹
Li(bim)	92(5)	40.0(6)	22.3(10)	154(5)
α-Na(bim)	-26	–13	343	304
β-Na(bim)	54(5)	-18.5(17)	183.7(4)	219(6)

Conclusion

We have successfully synthesized and characterized the crystal structures and thermal properties of Li(bim) and Na(bim). 3DED revealed that both materials crystallize in the orthorhombic crystal system, forming closely related layered coordination networks. DSC and VTXRPD revealed that both Li(bim) and Na(bim) melt above 450 °C. Notably, Na(bim) undergoes an additional displacive phase transition from an ordered α -phase to a dynamically disordered β -phase at approximately 166 °C. Li(bim) exhibits positive thermal expansion along all principal axes within the studied temperature range. In contrast, α -Na(bim) displays the very rare phenomenon of area NTE, due to large amplitude lattice vibrations orthogonal to the layer plane of the coordination network. These vibrations also drive the $\alpha \rightarrow \beta$ phase transition in Na(bim), resulting in a significant change in the coordination environment of the Na⁺ ions from close to square planar in the α -phase to more tetrahedral in the dynamically stabilized β -phase. As a result, Na(bim) switches from strong area NTE in the α -phase to linear NTE in the β -phase.

This study underscores the influence of the differing ionic radii of Li⁺ and Na⁺ on the structural and thermal properties of their respective benzimidazolate compounds. Na(bim) exhibits weaker metal-nitrogen bonds compared to Li(bim), consistent with its lower melting temperature. These structural variations lead to distinct thermal behaviors, with Na(bim) displaying complex thermal expansion characteristics, unlike the consistently positive thermal expansion observed in Li(bim). Due to the markedly

different thermal expansion behaviors of the β -Na(bim) and Li(bim) phases, the presence of a low-temperature α -Na(bim)-like phase of Li(bim) is considered unlikely.

Overall, this research provides valuable insights into the structural dynamics and thermal properties of alkali metal benzimidazolates, contributing to a deeper understanding of these materials and their potential applications. The discovery of strong area NTE in α -Na(bim), associated with large magnitude transverse vibrations, provides a guide for the design of this unusual property in other layered coordination networks. Moreover, the accessible liquid phase of Li(bim) and Na(bim) opens up new possibilities for their use as fluxes in the preparation of various vitreous composite materials. Specifically, these compounds could serve as effective network modifiers in the preparation of MOF and coordination polymer glasses.⁴⁷

Materials and Methods

All chemicals and solvents used in the synthesis were purchased from commercial sources. The benzimidazole was dried by resublimation at 100 °C under dynamic vacuum (10⁻³ mbar) overnight prior to the syntheses.

Synthesis of Li(bim)

1.5 g (12.7 mmol) of dry benzimidazole (Hbim) was dissolved in 55 mL of dry tetrahydrofuran (THF) in a purged Schlenk flask (250 mL) under constant argon flow. The solution was then cooled to approx. -70 °C and 4.5 mL (11.5 mmol) *n*-butyllithium (2.5 M in *n*-hexane) was slowly added using a syringe. The cooling bath was removed, and the solution was allowed to warm up to room temperature (25 °C) while stirring overnight. The next day the mother liquor was decanted from the precipitate, the solid was washed with dry *n*-hexane (1 x 40 mL) and dried at 100 °C under a dynamic vacuum for 2 h. Subsequently, the solid was heated to 250 °C for 3 h under a dynamic vacuum to remove any excess Hbim. Li(bim) was obtained as a white powder and stored in a glovebox under Ar atmosphere (yield 1.15 g, 81%).

Synthesis of α-Na(blm)

1.5 g (12.7 mmol) of dry Hbim was dissolved in 30 mL of dry THF in a purged Schlenk flask (250 mL) under constant argon flow. The solution was cooled with an ice bath and 6 mL (12.0 mmol) of sodium hexamethyldisilazane (NaHMDS, 2 M in THF) was added under Ar flow. The ice bath was removed, and the reaction mixture was allowed

to warm up to room temperature under stirring for 1 h. The yellow solution was filtered through a syringe filter (PTFE, 0.2 μ m) and transferred into another Schlenk flask (250 mL). 40 mL of dry *n*-hexane was added to form a white precipitate. The suspension was stored in a fridge at 8 °C overnight. Subsequently, the supernatant fluid was removed, and the white powder was washed with dry *n*-hexane (2 x 20 mL). After solvent removal under dynamic vacuum at 100 °C for 2 h, the solid material was transferred to a Schlenk-tube which was introduced to a tube furnace and heated at 280 °C for 3 h under dynamic vacuum to remove any excess Hbim. α -Na(bim) was obtained as a light-yellow powder and stored in a glovebox under Ar atmosphere (yield 1.43 g, 85%).

X-ray powder diffraction (XRPD)

XRPD measurements were performed at Beamline BL9 at DELTA (Dortmunder Elektronenspeicherring-Anlage, Dortmund, Germany) with a monochromatic X-ray beam ($\lambda = 0.4603$ Å) using a Dectris Pilatus 100K detector in an angular range from 2° – 35° (2 Θ) and a capillary rotor. The thoroughly ground sample material was filled in a borosilicate capillary (1.0 mm diameter) in a glovebox under an inert atmosphere (N₂) and sealed using epoxy glue (UHU Schnellfest).

Variable temperature (VT)XRPD experiments were conducted at beamline I15-1 at DLS (Diamond Light Source, UK) using a monochromatic X-ray beam ($\lambda = 0.161669$ Å), a Perkin Elmer XRD 4343 CT 2D plate detector, a capillary rotor and a hot air blower for adjusting the sample temperature. The finely ground sample material was filled in a borosilicate glass capillary (1.0 mm outer diameter) and sealed using epoxy glue (UHU Schnellfest) in a N₂-filled glovebox.

Data integration and processing were performed in DAWN 2.30.0.^{48,49} Structureless profile fits (Pawley method⁴⁰) as well as the Rietveld Refinement⁴⁴ were performed using the routines provided by the TOPAS-academic v6 software package.⁵⁰

3D Electron Diffraction (3DED)

The samples were handled in an argon-filled glovebox and prepared by sprinkling the powders onto holey carbon grids. The prepared grids were then loaded into a JEOL vacuum transfer holder and inserted into the TEM column. 3DED data were collected using a JEOL JEM2100 TEM, equipped with a Timepix detector from Amsterdam Scientific Instruments, while continuously rotating the crystal at 0.45° s⁻¹. The

experiments were carried out using Instamatic,⁵¹ with initial data assessment, as well as data reduction and merging (a single dataset for the lithium phase and 6 datasets for the sodium phase) being performed in *edtools* and XDS, respectively.^{52,53} The acquired intensities were then used to solve the structure of each phase using SHELXT,⁵⁴ and refined using SHELXL,⁵⁵ with electron scattering factors as previously published by Peng.⁵⁶ From the 3DED data, all non-hydrogen atoms could be located in the initial structure solution from SHELXT.

Simultaneous Thermogravimetric and Differential Thermal Analysis (STA)

STA was performed on a Discovery SDT 650 instrument from TA Instruments under a constant nitrogen flow or airflow of 100 mL min⁻¹. For the measurement, a small amount (~10 mg) of the powdered sample was placed in a 90 μ L alumina crucible in a glovebox with N₂ atmosphere. The thus prepared sample was removed from the inert atmosphere and quickly transferred into the STA instrument where it was heated with a constant heating rate of 10 °C min⁻¹ in a range from 50 °C to 800 °C (N₂ flow) or 1200 °C (airflow). In the latter case, the sample was held at the maximum temperature isothermally for 5 min to ensure complete thermal decomposition. Data evaluation was carried out in TA instruments TRIOS version 5.1.1.46572.

Differential Scanning Calorimetry (DSC)

DSC measurements were measured on a DSC25 from TA instruments. The samples were ground thoroughly and placed in a hermetically sealed aluminium crucible under N₂ atmosphere. All experiments were carried out under constant N₂ flow (50 mL min⁻¹) in a temperature range from 50 °C to approx. 500 °C with a constant heating and cooling rate of ± 10 °C min⁻¹. Data evaluation was carried out in TA instruments TRIOS version 5.1.1.46572. Temperature and enthalpy calibration was performed with an indium standard. The integrals of the heat flow curves are given as enthalpies ΔH even though the measurements were performed under hermetic conditions (*V* = constant) since it is generally assumed that enthalpies ΔH and internal energies ΔU are similar for processes involving only condensed phases.⁵⁷

Nuclear Magnetic Resonance (NMR) Spectroscopy

Solution ¹H NMR and ²⁹Si INEPT (insensitive nuclei enhanced by polarisation transfer) NMR spectroscopy was performed on a Bruker DPX-300, DPX 500 or Agilent DD2 500

spectrometer. The crystalline material was dissolved in DMSO- d_6 (0.5 mL) and DCI/D₂O (35 wt%, one drop, <0.1 mL). Data processing was performed in MestReNova (v14.2.0). The data was referenced to the residual proton signals of DMSO- d_6 and all chemical shifts are given relative to tetramethylsilane.

Fourier Transform (FT)IR spectroscopy

Infrared spectra were collected on a Spectrum 3 FTIR spectrometer in a range from $4000 - 400 \text{ cm}^{-1}$. A Gladi ATR-300 unit from Pike Technologies with a diamond crystal was used as an attenuated total reflectance (ATR) unit. During the measurement all samples were compressed with a stamp securing the sample on the diamond and an inert-gas (N₂) flow was put in place to minimize the samples' reaction with atmospheric water.

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Author Contributions

P.K. and L.R. synthesized the materials and conducted and analyzed the thermal analysis data and spectroscopic measurements. 3DED data collection and analysis was performed by E.S.G. and A.K.I.. P.K. collected and analyzed the XRPD data. R.P. performed the Rietveld refinement of β -Na(bim). The manuscript was written by P.K. and S.H. with contributions from the other authors.

Supporting Information

Solution ¹H NMR spectra, simultaneous thermogravimetric and differential thermal analysis (STA) curves, differential scanning calorimetry (DSC) thermograms, 3D electron diffraction (3DED) data, optical microscopy images, infrared (IR) spectra and X-ray powder diffraction (XRPD) data.

Accession Codes

CCDC 2364871-2364872 and 2365470 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

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