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Article

Experimental Investigation of Thermodynamic Stabilization in Boron Imidazolate Frameworks (BIFs) Synthesized by Mechanochemistry

Gerson J. Leonel, Cameron B. Lennox, Manuel Scharrer, K Jayanthi, Tomislav Friščic,* and Alexandra Navrotsky*



imidazolate frameworks (BIFs), which are synthesized by mechanochemistry. The topologically similar frameworks employ the same tetratopic linker based on tetrakis-(imidazolyl)boric acid but differ in the monovalent cation metal nodes. This permits assessment of the stabilizing effect of metal nodes in frameworks with sodalite (SOD) and diamondoid (*dia*) topologies. The enthalpy of formation from endmembers (metal oxide and linker), which define thermodynamic stability of the structures, has been determined by use of acid solution calorimetry. The results show that heavier metal atoms in the node promote greater energetic stabilization of denser structures. Overall, in BIFs the relation between cation descriptors (ionic radius and electronegativity) and thermodynamic stability depends on framework topology. Thermodynamic stability increases with the metallic character of the cation employed as the metal node, independent of the framework topology. The results suggest unifying aspects for thermodynamic stabilization across MOF systems.



INTRODUCTION

Metal organic frameworks (MOFs) are self-assembled, highly porous structures composed of metal-containing secondary building units linked by organic ligands.^{1,2} This field of reticular chemistry has led to development of subclasses of MOFs, including zeolitic imidazolate frameworks (ZIFs) and boron imidazolate frameworks (BIFs).^{3,4} These materials continue to increase in popularity due to the facile manipulation of their electronic and transport properties, through the use of appropriate metal-ligand combinations.⁵ This permits fine-tuning of material properties to meet current and future technological demands.^{7,8} To date, MOFs have promising application in quantum dot semiconductors, biomedical imaging, and molecular sieving.⁹⁻¹¹ Additionally, recent work in actinide science has explored developing MOFs based on f-block elements (uranium, thorium, and plutonium), which have potential use in nuclear energy and waste management applications.^{12–14}

Currently, there have been reports on the synthesis of tens of thousands (~90,000) of different MOF structures, and this number is ever-increasing, as more studies investigate the synthesis of frameworks with desired properties.^{15,16} Common routes for the synthesis of frameworks include solvothermal syntheses and mechanochemistry.^{4,17–19} To reduce possible negative environmental impact from use of large amounts of solvents, recent work continues to explore alternative synthesis approaches.²⁰ Solvent-free synthesis can be achieved by use of mechanochemical synthesis methods like ball-milling, including liquid-assisted grinding; hence, the synthesis of MOFs is no longer limited to reactants that must be completely dissolved in liquid media.²¹ Fundamentally, the reaction conditions in the solvothermal and mechanochemical approaches are different, which has in some cases enabled the observation of materials and topologies so far only accessible by mechanochemistry.^{3,4,22} The sodalite (SOD) and diamondoid (*dia*) topologies are often observed across both ZIFs and BIFs.^{4,22} Structures in the SOD topology are typically much more porous compared to denser frameworks in the *dia* topology.^{22,23} Past work shows that the difference in the thermodynamic stability of may be associated with differences in density of the frameworks with longer grinding leading to denser and more stable phases.^{3,22,24}

Previous works investigated stability trends in MOFs.²⁵ The results indicate that in MOFs, thermal as well as thermodynamic stability is determined by both the coordination number and local environment around the metal.^{2,3,25–27} Most studies explore the synthesis and potential application of novel structures;^{28,29} nonetheless, current knowledge of structure–

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Figure 1. Illustration of (a) the BIF ligand $[B(Meim)_4^-]$, (b) structure of a BIF in the sodalite (SOD) topology, and (c) structure of a BIFs in the diamondoid (*dia*) topology (pink = boron, blue = nitrogen, black = carbon, , and green = metal centers).



Figure 2. Experimental and simulated powder X-ray diffraction patterns of herein investigated BIFs, from top-to-bottom: (a) measured for dia-AgB(MeIm)₄ and (b) simulated for dia-AgB(MeIm)₄ (CSD: CAHWAN); (c) measured for SOD-AgB(MeIm)₄ and (d) simulated for SOD-AgB(MeIm)₄ (CSD: CAHWAN01); (e) measured for SOD-CuB(MeIm)₄ and (f) simulated for SOD-CuB(MeIm)₄ (CSD: MOXJOZ); (g) measured for dia-LiB(MeIm)₄ and (h) simulated for dia-LiB(MeIm)₄ (CSD: MOXKUG).

property relationships in MOFs is scarce, and this is an important consideration for the long-term application of these materials. Various studies have explored computational routes to address this problem; however, experimental data validating the results from machine learning and/or atomistic models are lacking.^{30–33} Additionally, since thermodynamic stability is an important factor in the modular design of MOFs, it is essential to identify structural descriptors in the linkers and metal centers contributing to greater thermodynamic stability in MOFs. This is possible through development of a unifying framework for systematic stabilization of MOFs across different topologies and dimensions (2-dimensional (2D) and 3-dimensional (3D)).

Previous works employed calorimetric methods to investigate the thermodynamic stability of MOFs, including ZIFs employing ditopic 2-methylimidazolate (MeIm⁻) ligands.^{2,3,27} In this work, we investigate the stability of four BIFs based on tetrakis(imidazolyl)boric acid (H[B(MeIm)₄]) ligand (see Figure 1a): *dia*-LiB(MeIm)₄, *dia*-AgB(MeIm)₄, SOD-CuB-(MeIm)₄, and SOD-AgB(MeIm)₄. The structures employ the same organic linker but different metal nodes. This systematic investigation permits identification of structural descriptors in metal atoms as well as quantitation of their stabilizing effect across different framework topologies. The chemical and structural characterization of the samples is done by Fouriertransform infrared spectroscopy (FTIR), thermal analysis (TGA-DSC), and powder X-ray diffraction (XRD). The thermochemical analyses employ enthalpies of formation. This is the first work employing calorimetry to explore the thermodynamic stability of BIFs based on tetratopic linkers (Figure 1a). This is a valuable addition to the current MOF thermodynamic database, which permits expansion of current knowledge on structure–stability relationships in BIFs and other MOFs, as well as validation of general trends suggested from previous DFT calculations.⁴

EXPERIMENTAL METHODS

Syntheses. All BIFs are synthesized through the mechanochemical route that was previously reported,⁴ and a detailed description of the synthesis procedure and characterization is provided as Supporting Information.

Thermodynamic Measurements. Enthalpies of formation are calculated using dissolution enthalpies obtained by room temperature acid solution calorimetry in a CSC4400 isothermal microcalorimeter. Dissolution of KCl is employed for calibration of the calorimeter. This is a well-established technique, and the procedure has been employed for investigation of other MOFs and similar materials.^{3,34} Previous works describe the calorimetric experiments in more detail.^{3,35}

RESULTS AND DISCUSSION

XRD patterns are shown in Figure 2. The experimental patterns are consistent with those calculated using CCDC Mercury software based on published crystallographic data for dia-LiB(MeIm)₄, dia- AgB(MeIm)₄, SOD-CuB(MeIm)₄, and SOD-AgB(MeIm)₄ structures.⁴ The measured Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra (Supporting Information) are consistent with boron–imidazolate as well as imidazolate–metal bonds, which are expected in BIFs. Thermogravimetric analysis (TGA) enables quantitation of metal content in the frameworks, and the results are consistent with the expected stoichiometry (see the Supporting Information).

Thermodynamics of BIFs and Other MOFs. Current knowledge of the thermodynamics of MOFs is based on previous studies on frameworks composed of oxygen-based linkers, including paddlewheel-type MOFs, as well as structures employing ditopic nitrogen-based linkers, such as ZIFs.^{2,3} The present work aims to expand upon these studies, investigating the thermodynamic stability of BIFs. In the present study, thermodynamic analysis employs enthalpies of dissolution (ΔH_{dis}) of the frameworks and endmembers (monovalent metal oxide as well as linker). Li₂O and Cu₂O are soluble in 5 N HCl, and the thermochemical cycle shown in Table 1

Table 1. Thermodynamic Cycles for the Enthalpy of Formation of $MB(MeIm)_4$ Structures, Where $M = Cu^+$ or Li^{+a}

Reaction	$\Delta H (kJ mol^{-1})$
$^{1}/_{2}M_{2}O~(s,298~K)$ + HB(MeIm)_{4} (s,298~K) \rightarrow MB(MeIm)_{4} (s, 298~K) + $^{1}/_{2}H_{2}O~(l,298~K)$	$\Delta H_{\rm f} = ?$
$\rm MB(MeIm)_4~(s,~298~K) \rightarrow M^+~(aq,~298~K) + B(MeIm)_4$ ^ (aq, 298 K)	ΔH_1
$\rm M_2O~(s,~298~K) + 2H^+~(aq,~298~K) \rightarrow 2M^+~(aq,~298~K) + H_2O~(aq,~298~K)$	ΔH_2
HB(MeIm) ₄ (s, 298 K) \rightarrow H ⁺ (aq, 298 K) + B(MeIm) ₄ $^-$ (aq, 298 K)	ΔH_3
H_2O (l, 298 K) \rightarrow H_2O (aq, 298 K)	ΔH_4
$\Delta H_{\rm f} = -\Delta H_1 + {}^{1}/{}_{2}\Delta H_2 + \Delta H_3 - {}^{1}/{}_{2}\Delta H_4$	$\Delta H_{ m f}$
^{<i>a</i>} l, liquid phase; s, solid phase; aq, aqueous.	

permits the calculation of enthalpies of formation of the respective frameworks (LiB(MeIm)₄ and CuB(MeIm)₄). In contrast, Ag₂O precipitates as AgCl in 5 N HCl ($-185.32 \pm 0.60 \text{ kJ}\cdot\text{mol}^{-1}$), and therefore the thermodynamic cycle

describing the formation of SOD- and *dia*-AgB(MeIm)₄ BIFs is modified accordingly (see the Supporting Information).

The results are summarized in Table 2. Enthalpies of formation $(\Delta H^{\circ}_{\rm f})$ permit determination of the relative thermodynamic stability of different MOFs. In reactions involving only crystalline solids, enthalpy is the dominant term in the free energy as the entropy term is usually small. Since the energetics of forming these materials is dominated by the enthalpic term, a more exothermic enthalpy of formation typically corresponds to lower free energy, and thus, greater thermodynamic stability.

Table 2 shows that BIFs have enthalpies of formation between -61 and -99 kJ·mol⁻¹ (relative to the monovalent metal oxide and linker). These are much more exothermic than values for ZIFs, which typically range between -30 and -4 kJ· mol⁻¹, as seen in ZIFs employing MeIm⁻ linkers.³ This can result from a difference both in chemistry and in structure of BIFs compared to ZIFs. In terms of chemistry, the formation reaction can be viewed as an acid-base neutralization, where the acidic linker reacts with the basic oxide to form a metal oxygen linkage and release water. The monovalent oxides in BIFs are stronger bases than ZnO. The boron-containing linker may also be a stronger acid than its boron-free counterpart. The larger difference in acid-base character will make the neutralization reaction more exothermic/favorable (see Figure 3). It is possible that the introduction of boron linker centers stabilizes the frameworks. This may result from several factors, including less steric hindrance in bonds between metal centers and organic linkers, different sizes and charges of cations, differences in chemical bonding, or differences in electron distribution and bond angles in the linker. Our previous study has reported first-principles calculations of relative stabilities of herein studied SOD and *dia* frameworks.⁴

Despite differences in the magnitude of enthalpies of formation relative to endmembers, increase in framework density appears to be a unifying framework descriptor for thermodynamic stabilization across both BIF and ZIF systems (see Figure 3).^{22,24} The thermodynamic analysis of Ag-based frameworks (Table 2) points to greater thermodynamic drive for the formation of *dia*-AgB(MeIm)₄ compared to SOD-AgB(MeIm)₄. This is consistent with results from previous ZIF studies, which indicate that the porous SOD-topology polymorphs are metastable relative to the denser *dia*-topology counterpart frameworks.^{3,22} It is also qualitatively consistent with the conclusions of our previous computational study based on periodic density-functional theory (DFT) calculations,⁴ although the enthalpy difference between *dia*- and

Table 2. Ent	halpies of	Dissolution i	n 5 N HCl	at 25 °C	C and En	thalpies o	f Formation	of BIFs	from the	Metal	Oxide and	Linker

Sample	BET Surface Area (m ² ·g ⁻¹)	$\Delta H_{ m dis}~(m kJ\cdot mol^{-1})$	$\Delta H^{\circ}_{\rm f} \ (\rm kJ \cdot mol^{-1})$
HB(MeIm) ₄		-144.42 ± 0.43 (4)	
H_2O^{22}		-0.5	
Li ₂ O ^a		-254.036 ± 0.27 (5)	
Ag ₂ O		-185.32 ± 0.60 (6)	
Cu ₂ O		-246.80 ± 0.59 (5)	
dia-LiB(MeIm) ₄		-176.82 ± 0.66 (5)	-94.35 ± 0.97
dia-AgB(MeIm) ₄		-137.54 ± 0.62 (5)	-99.28 ± 0.96
SOD-AgB(MeIm) ₄	1020 ⁴	-186.93 ± 0.28 (5)	-49.89 ± 0.79
SOD-CuB(MeIm) ₄	935 ⁴	$-206.48 \pm 0.72 (5)$	-61.07 ± 1.02

^aEnthalpy of dissolution of Li_2O is calculated from dissolution of Li_2CO_3 . Error is reported as two standard deviations from the mean. Value in parentheses represents the number of experiments.



Figure 3. Comparison of energetic landscape in BIFs and ZIFs, based on energetics of formation from endmembers (metal oxide and ligand). The figure highlights the greater stability of BIFs relative to endmembers. Overall, for both ZIFs and BIFs, the more dense *dia* topology structures present greater stability than their SOD-topology counterparts.

SOD-topology polymorphs of $AgB(MeIm)_4$ is herein measured to be ca. 50 kJ mol⁻¹, which is significantly different from the previously calculated ca. 9 kJ mol⁻¹ difference. The reason for this difference remains unclear. Overall, it is likely that an increase in framework density is a universal descriptor for enhanced stabilization across all MOFs (not just BIFs and ZIFs), which would imply that any metal–ligand combination could be stabilized by accessing denser polymorphs.

To further explore the possible systematics in the stabilizing effect of metal nodes in BIFs, we investigate correlations between metal descriptors (electronegativity, ionic radius, metallic character) and their corresponding thermodynamic trends across different framework topologies. The results in Table 2 highlight three main points: (1) In BIFs: heavier metal atoms promote further stabilization of denser polymorphs, (2) denser polymorphs show less destabilization from choice of metal, and (3) the stabilizing effect of metal nodes increases with metallic character of the cation. Additionally, for the porous BIF structure in the SOD topology, monovalent Cu nodes promote the greatest energetic stability.

The Pauling electronegativity of Li (0.98),³⁶ Cu (1.9),³⁷ and Ag $(1.93)^{38}$ influences the ability of metal nodes to pull electrons from the linker, and this affects metal–ligand bond strength and length. An optimal combination of strong (short) bonds with reduced lattice strain is desirable for favorable interactions at the interfaces between the metal nodes and the organic linkers. In the SOD topology, employing Ag⁺ instead of Cu⁺ results in a thermodynamic penalty of ~12 kJ·mol⁻¹. This indicates significant destabilization of the porous framework with only a minor increase in the electronegativity of metal atoms, perhaps due to lattice strain, which is destabilizing.^{39–41} In contrast, in the *dia* topology, the effect of electronegativity appears to be opposite and more subtle, as

significant dissimilarities in the electronegativity of Ag^+ and Li^+ only result in an ~5 kJ·mol⁻¹ enthalpy difference in *dia*-BIFs (see Table 2). This suggests only minor differences in the thermodynamic stability of denser BIF polymorphs arising from choice of metal.

The ionic radius may also impact the interaction between metal atoms and organic ligands, Li = 73 pm,⁴² Cu = 77 pm,^{43,44} and Ag = 115 pm.^{43,45} We define metallic character as the ratio of electronegativity to ionic radius with Li = 0.013, Cu = 0.025, and Ag = 0.016. The measured enthalpies show a positive correlation between metallic character and the stabilizing effect of metal nodes for all framework topologies. Other works investigating the thermodynamic stability of MOF-74 frameworks, using oxygen-based linkers, suggest similar correlations.²⁷ These regularities may point to metallic character as another unifying descriptor for increased thermodynamic stabilization across MOFs, independent of linker environment (oxygen or nitrogen) or coordination number.

It is known that other metals can be employed as nodes in BIF structures, $^{46-48}$ and the results in this work shed light on possible constraints for increased thermodynamic stabilization. In BIFs, metal (M)–nitrogen (N) as well as boron (B)– nitrogen (N) (in the tetratopic ligand) bonds (Figure 1a) should be strong enough to prevent collapse of the framework to other more thermodynamically favorable structures. There may exist an ideal electronegativity and ionic radius of metal atoms to make the most stable BIFs. Deviations from ideal metal (M)–nitrogen (N) bond length and/or (strength) are expected to result in thermodynamic penalty. This places restrictions on the favorable electronegativity of the metal is lower than optimum, the M–N bond strength will be

suboptimal (weaker), and likely less stable. In contrast, metal atoms with electronegativity greater than the optimum (depending on topology), may form shorter and/or stronger M-N bonds, but this may be at the cost of decreased electron density around the B-N bonds (weakening of bonds between boron linker center and nitrogen). This is important, since the electron density in the linker influences framework stability.³ It should also be highlighted that suboptimally shorter M-N bonds can result in increased lattice strain, especially in SODtopology BIFs, as suggested in this work. The strength of both the B-N and M-N bonds must be considered in the rational design of stable frameworks. The present results indicate most favorable incorporation of metal atoms with electronegativities greater than \sim 0.98 for BIFs in the *dia* topology, and lower than 1.93 in the porous polymorph (SOD). It should be stressed that other electronic and magnetic factors may affect the trends identified thus far. Additionally, it is likely that some of the trends herein observed (e.g., electronegativity limit for increased stabilization) may be system-dependent and may not translate to other systems employing different metalligand combinations.

Practical Implications. The surface area of MOFs can be well beyond that of activated carbon, which makes them desirable candidates for molecular sieving and storage; however, hydrolysis of the frameworks is a challenge. 49,50 The term "stability" is often used in two different senses, one indicating thermodynamic stability against some decomposition reaction and the other indicating kinetic persistence of the phase when it is exposed to aqueous media for a period of time under a given set of conditions, often without knowledge of the thermodynamics. The first case implies true stability controlled by thermodynamics, and the second implies kinetically slow decomposition, even if allowed by thermodynamics. It should be highlighted that the reverse of the formation reaction in Table 1 does not describe hydrolysis in BIFs; hydrolytic decomposition should form thermodynamically more stable products than the oxide and linker molecule. These hydrolysis products are likely dominated by metal hydroxides and hydrolyzed or decomposed linker molecules. Differences in the free energies of the hydrolysis reactions determine the thermodynamic propensity for framework degradation. The complexity of the possible hydrolysis reactions makes it difficult to unambiguously compute their energetics. Nevertheless, the added stability of hydroxides compared to oxides will make hydrolysis thermodynamically favorable, especially under basic conditions.

The BET surface area $(m^2 g^{-1})$ of mechanochemically synthesized SOD-AgB(MeIm)₄ and SOD-CuB(MeIm)₄ were previously reported to be 1020 and 935, respectively.⁴ The porous MOFs can be employed for gas adsorption applications.^{51,52} This and previous works indicate a trade-off between thermodynamic stability and surface area/porosity (adsorption capacity) of the structures.^{3,22} This is an important consideration as recent efforts continue to investigate gas storage in MOFs, especially the capture of CO₂.⁵³ Additionally, denser MOFs can display ferroelectric properties that are desirable for application in computer RAMs.^{54,55} The high thermodynamic stability of denser MOFs, including *dia*-BIFs may favor their long-term applications.

CONCLUSIONS

results confirm greater stability of all compositions with increasing density of the framework. In the denser *dia* topology, BIFs employing metal atoms with a larger ionic radius and higher electronegativity are thermodynamically more stable. Overall, across the SOD and *dia* topology, the thermodynamic stability of the BIFs increases with the metallic character of the nodes. The results suggest unifying systematics in the thermodynamic stabilization of BIFs and other MOF systems, leading to the ability to tailor, using thermodynamic constraints, stable structures with desirable properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c04164.

Materials and methods, Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy and thermogravimetric analysis (TGA) data, table of the thermochemical cycle (PDF)

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Notes

The authors declare no competing financial interest.

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