

Research Article

Ionothermal Synthesis of a Novel 3D Cobalt Coordination Polymer with a Uniquely Reported Framework: $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$

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The framework of $[\text{RMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (RMI = 1-alkyl-3-methylimidazolium, alkyl; ethyl (EMI); propyl (PMI); butyl (BMI)), which has uniquely occurred in ionothermal reactions of metal salts and H_3BTC (1,3,5-benzenetricarboxylic acid), an organic ligand, reappeared in this work. Ionothermal reaction of cobalt acetate and H_3BTC with $[\text{BMI}]\text{Br}$ ionic liquid as the reaction medium yielded the novel coordination polymer $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B2**). Similar ionothermal reactions with different $[\text{EMI}]\text{Br}$ and $[\text{PMI}]\text{Br}$ as the reaction media have been previously reported to produce $[\text{EMI}]_2[\text{Co}_3(\text{BTC})_2(\text{OAc})_2]$ (compound **A1**) and $[\text{PMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B1**), respectively. In contrast with the trinuclear secondary building unit of **A1**, the framework structure of **B1** and **B2** consists of dinuclear secondary building units in common, but with subtle distinction posed by the different size of the incorporated cations. These structural differences amidst the frameworks showed interesting aspects, including guest and void volume, and were used to explain the chemical trend observed in the system. Moreover, the physicochemical properties of the newly synthesized compound have been briefly discussed.

1. Introduction

The rising demands for new materials with befitted properties for applications in numerous fields of science and industry [1–3] have led to development and advancements of novel synthesis methods [4–10]. Ionothermal synthesis, where ionic liquids are used both as solvents and templates [11], has been recently deployed for preparation of novel structures [12, 13] amidst a great attention attributed to its unique and pragmatic physicochemical properties [11], namely, those discussed hereafter and many more [14–16]: high thermal stability [17], negligible vapor pressure [18], environmentally friendliness [19], and, most interestingly, its ability to finely tune the reaction environment by changing the cation and anion of the ionic liquid and ultimately enabling systematic approach to the final product [20, 21]. Despite such attractiveness of ionothermal synthesis and its expandability that has already been demonstrated with novel structures of various classes including zeolites [12, 13], zeotype frameworks [12, 22–24],

and metal-organic frameworks or MOFs [20, 21, 25], the methodology has not been extensively employed [21], leaving a vast number of different reaction conditions for future research. The unique advantages of ionothermal synthesis may be fully practiced only when enough experiments have been carried out with various circumstances to produce a sizable number of frameworks.

We herein report a novel 3D cobalt coordination polymer $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B2**), which has been ionothermally prepared with $[\text{BMI}]\text{Br}$ as the solvent. Its framework is very rare in literature, previously being only uniquely exemplified by $[\text{PMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B1**), a polymer obtained from a reaction analogous to ours, but with $[\text{PMI}]\text{Br}$ as the solvent [26]. On the contrary, another analogous reaction with $[\text{EMI}]\text{Br}$ as the solvent yielded a polymer with a notably different framework, $[\text{EMI}]_2[\text{Co}_3(\text{BTC})_2(\text{OAc})_2]$ (compound **A1**) [27]. Moreover, attempts have been made to synthesize novel polymers with $[\text{PEMI}]\text{Br}$ and $[\text{HMI}]\text{Br}$ and acquired

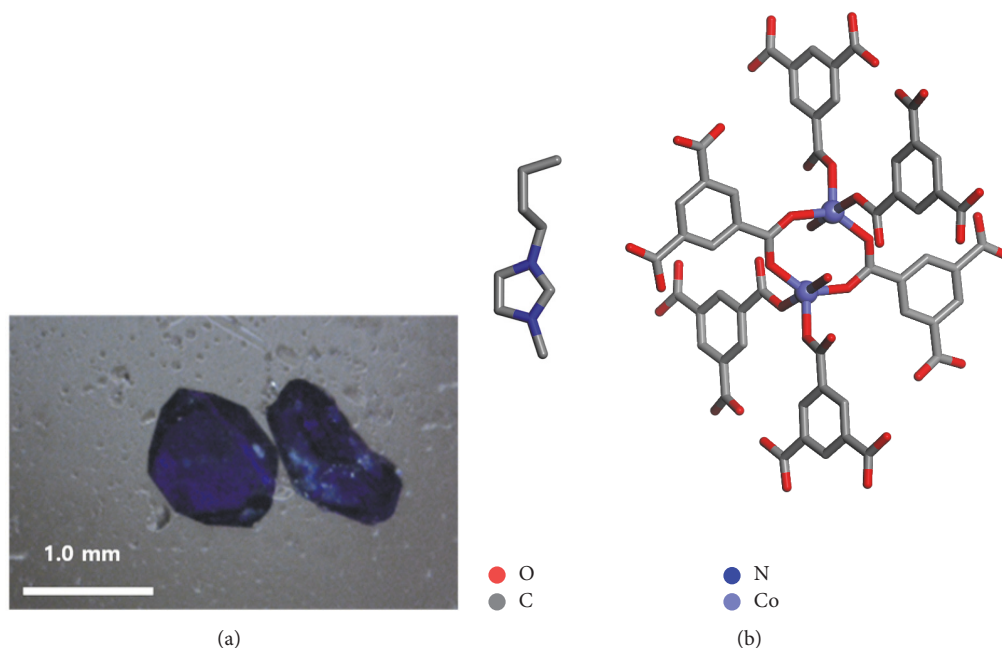


FIGURE 1: (a) Crystal image of synthesized $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ crystals. (b) Molecular models depicting the incorporated cations and the secondary building units (SBUs) of $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$.

pink amorphous solids. In order to provide explanations to the trend introduced above, the framework of the novel compound $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B2**) will be thenceforth examined from various aspects in relation to that of $[\text{EMI}]_2[\text{Co}_3(\text{BTC})_2(\text{OAc})_2]$ (compound **A1**) and $[\text{PMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B1**).

2. Experimental

2.1. Crystal Preparation. For the preparation of $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B2**), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (3.0 mmol, 0.7472 g) and H_3BTC (2.0 mmol, 0.4203 g) were placed altogether in a 23 mL Teflon-lined stainless-steel autoclave with $[\text{BMI}]\text{Br}$ (20 mmol, 4.3824 g). The mixture was gradually heated in a furnace for 3 hours to reach the reaction temperature of 150°C . The temperature was held still for 3 days and slowly cooled to room temperature for 5 hours. The obtained deep blue crystals (Figure 1(a)) were filtered, washed with ethanol, and naturally dried for purification. All chemicals including ionic liquids (ILs) were commercially purchased from Chem. Tech. Research Incorporation (C-TRI) and Sigma-Aldrich Chemical Company and used without further purification.

2.2. Crystal Structure Analysis. Crystallographic data of obtained crystals were collected at -100°C on Bruker Smart Breeze diffractometer in different locations including Pusan National University. Summary of crystallographic data for compound **B2** are given in Table 1 and further details of the crystal structure have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-1525180). For crystallographic comparison,

summarized data for compound **A1** and compound **B1** are also given in Table 1.

Powder X-ray diffraction (PXRD) data were recorded on a Rigaku Miniflex 600 diffractometer at 40 kV, 15 mA for $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of $5^\circ/\text{min}$, and a step size of 0.01° in 2θ .

3. Result and Discussion

The framework of compound **B2** imputes its understructure to the dinuclear unit built by connecting two cobalt atoms with six BTC^{3-} ligands as illustrated in Figure 1(b). The fundamental asymmetric unit of compound **B2** contains one cobalt (II) atom, one BTC^{3-} ligand, one $[\text{BMI}]$ cation, and a water molecule (Table 1). Each cobalt (II) atom is five-coordinated with four oxygen atoms from carboxylate groups of BTC^{3-} ligands and one from a water molecule in a distorted trigonal bipyramid geometry. BTC^{3-} ligands exhibit μ_4 coordination modes: two of the carboxylates exhibit monodentate coordination fashion and the remaining bidentate coordination fashion. Two symmetric cobalt (II) atoms are linked by two carboxylate groups exhibiting bidentate coordination mode, each from different BTC^{3-} ligands and form the $[\text{Co}_2(\mu_2\text{-COO})_2]$ core as in compound **B1** [26] (Figure 1(b)). Nevertheless, the distance between two neighboring cobalt (II) atoms is 3.53 \AA , which is slightly shorter than that of compound **B1**, 3.56 \AA [26], but such an arrangement with a long distance of 3.53 \AA still eradicates the possibility of direct interaction between them. The range of Co-O distance was measured to span from $1.9830(13) \text{ \AA}$ to $2.1314(14) \text{ \AA}$ (see Table 2), exhibiting the similar range of compound **B1** [26]. The 3D framework of compound **B2**,

TABLE 1: Crystallographic data for Co-BTC metal organic frameworks synthesized with [RMI]Br ionic liquids (RMI = EMI, PMI, BMI).

	[EMI] ₂ [Co ₃ (BTC) ₂ (OAc) ₂]	[PMI] ₂ [Co ₂ (BTC) ₂ (H ₂ O) ₂]	[BMI] ₂ [Co ₂ (BTC) ₂ (H ₂ O) ₂]
Empirical formula	C ₂₂ H ₁₂ Co ₃ O ₁₆	C ₁₆ H ₁₈ CoN ₂ O ₇	C ₁₇ H ₂₀ CoN ₂ O ₇
Fw	709.11	409.26	423.28
Space group	Pbca	P2(1)/n	P2(1)/n
Crystal system	Orthorhombic	Monoclinic	Monoclinic
A (Å)	14.2616(4)	11.279(10)	11.1946(5)
B (Å)	16.1525(5)	10.679(10)	10.7911(5)
C (Å)	16.4867(5)	15.428(14)	15.3026(8)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	95.276(14)	95.3550(10)
γ (deg)	90.00	90.00	90.00
Cell volume	3797.9(2)	1850.406	1840.52(15)
Z	4	4	4
T (K)	90(2)	273	173(2)
R factor	0.0323	0.0522	0.0183
Reference	[27]*	[26]*	This work

*The reference in the article.

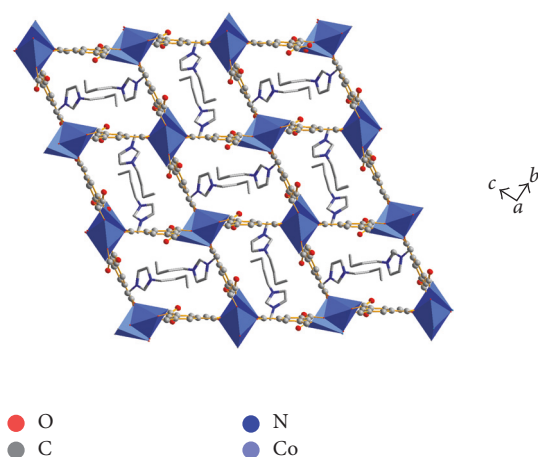


FIGURE 2: The 3D framework of [BMI]₂[Co₂(BTC)₂(H₂O)₂].

given by connecting cobalt (II) core with six BTC³⁻ ligands, has rhombic channels parallel to the crystallographic *a* axis (Figure 2). [BMI] cations of ionic liquids residing in the open channels as shown in Figure 2 behave as charge balancing species for the anionic framework.

The difference between type A framework, a trinuclear system, and type B frameworks, dinuclear system, becomes evident at their secondary building units, visually depicted at Figure S1 in Supplementary Material available online at <https://doi.org/10.1155/2017/3237247>, along with the subtlety in distinction between compound **B1** and compound **B2** [26, 27]. However, the [RMI] molecules were present as guests in all frameworks, suggesting a role played by the alkyl chains of differing lengths in determination of framework types.

To further account for the effect of guest molecules, Connolly surfaces and volumes have been calculated for their in situ conformations and for the cation pairs in the form of which the guests occur [28] (Figure 3). Note that

the [EMI] cations are so severely disordered in compound **A1** that reliable conformation data could not be obtained and therefore, data for [EMI] have been imported from isorecticular correspondent prepared with nickel in place of cobalt (CCDC number 719778) for better depiction of the trend. It has been discovered that the butyl chain of [BMI] molecule is considerably bent, making the volume of the molecule only slightly larger than [PMI] molecule compared to the increase in volume from [EMI] to [PMI]; the distance from the first carbon of the alkyl chain to the final carbon was 2.918 Å in compound **B2**, which is only slightly larger than 2.567 Å of compound **B1**. This indicates that the type B framework is stable for the cobalt-BTC system strong enough to cause the severe bending in the butyl chain of the guest molecule whilst the increase of guest volume from [EMI] to [PMI] posed the boundary between framework A and B. Nevertheless, the scarcity of the framework in systems of other metal elements suggests such a favor is limited specifically to the cobalt system (see Table S1).

It is apparent that increasing guest volume will exert a pressure on the framework to the direction of expanding its free volume. Occupied volume and free volume have been calculated for the three compounds and yielded a result corresponding to the expectation, but only partially (Figure S2). The free volume ratio was determined to be nearly the same for compounds **B1** and **B2**, suggesting the rigidity of the framework with respect to the change of free volume ratio. This result accords with the bent conformation of the [BMI] cation in compound **B2** and the failure to produce crystalline frameworks in reactions using [PEMI]Br and [HMI] in place of [BMI], respectively; this framework remains invariant over a range of synthesizing environment and such invariance may at minimum be partially attributed to the absence of any other framework that could rise from this range of synthesizing environment. Figure 4 summarizes the data regarding the occupied volume, the free volume, the guest volume, and the volume of the cation pairs that the guests found in structure.

TABLE 2: Selected bond lengths [\AA] and bond angles [deg] of $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$.

Co(1)-O(2)#1	1.9830(13)	O(2)#1-Co(1)-O(5)#3	91.75(6)
Co(1)-O(1)	1.9904(14)	O(1)-Co(1)-O(5)#3	93.06(6)
Co(1)-O(3)#2	2.0116(13)	O(3)#2-Co(1)-O(5)#3	89.12(6)
Co(1)-O(5)#3	2.0524(13)	O(2)#1-Co(1)-O(7)	84.43(6)
Co(1)-O(7)	2.1314(14)	O(1)-Co(1)-O(7)	92.24(6)
O(2)#1-Co(1)-O(1)	138.72(6)	O(3)#2-Co(1)-O(7)	89.40(6)
O(2)#1-Co(1)-O(3)#2	117.73(6)	O(5)#3-Co(1)-O(7)	174.69(6)
O(1)-Co(1)-O(3)#2	103.32(6)		

Symmetry transformations: #1: $-x + 2, -y + 1, -z$; #2: $-x + 3, y + 1/2, -z + 1/2$; #3: $x - 1/2, -y + 1/2, z - 1/2$.

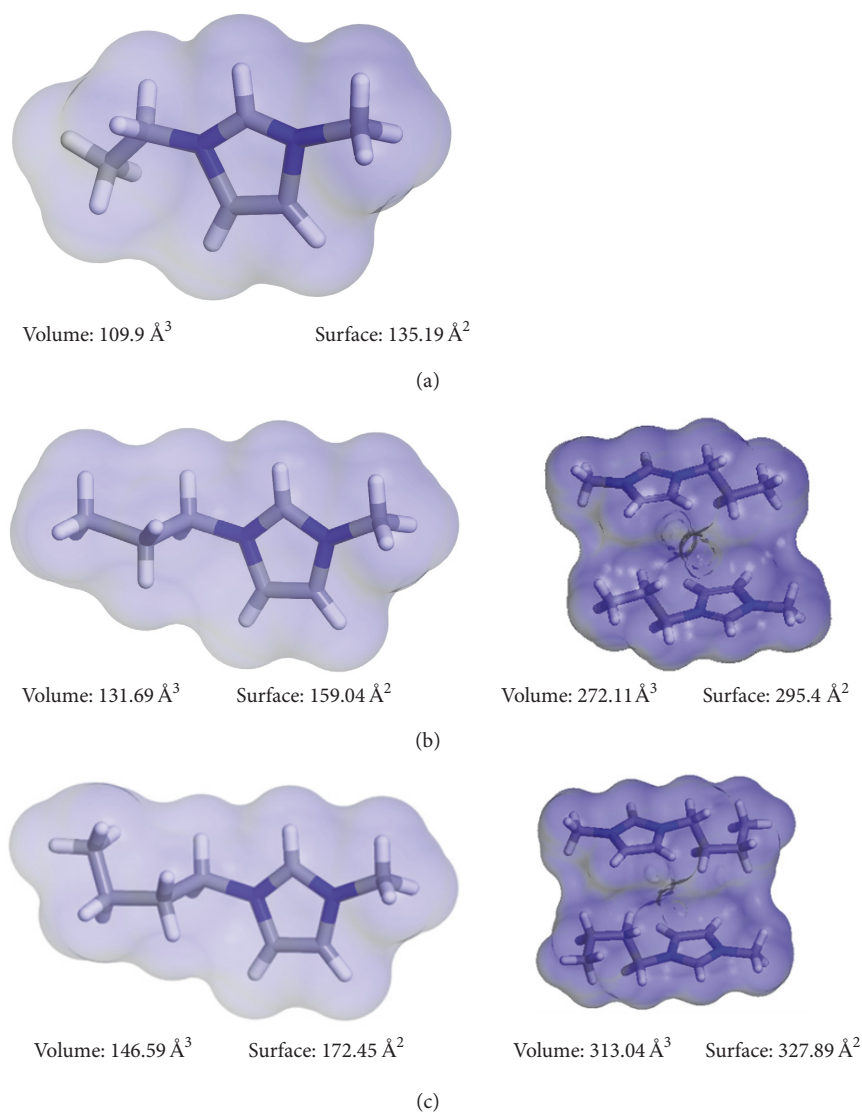


FIGURE 3: Connolly surfaces of the incorporated cations in their in situ conformations (left) and the cation pairs (right): (a) 1-ethyl-3-methylimidazolium, with data borrowed from the isorecticular correspondent prepared with nickel in place of cobalt, (b) 1-propyl-3-methylimidazolium, and (c) 1-butyl-3-methylimidazolium [28]. (Volume and surface area values have been calculated with the grid interval of 0.15 \AA and the Connolly radius being 1.0 \AA .)

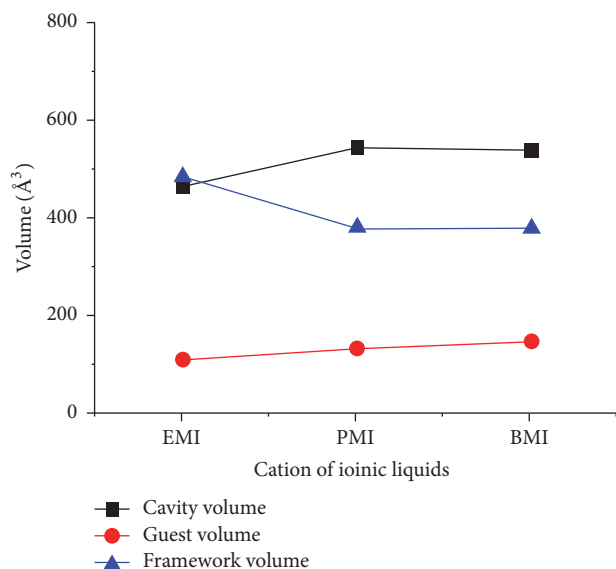


FIGURE 4: Plots of various calculated volumes per cation in each of the ionic liquids, where the data for guest and guest pair volume for EMI have been imported from the isorecticular correspondent prepared with nickel in place of cobalt for better illustration of the increasing trend of the guests.

Lastly, physicochemical properties of compound **B2** have been explored from a variety of scopes including those that have not been practiced for compound **B1** upon its synthesis. Several analyses were additionally performed to confirm the incorporation of ligands and metals. Infrared absorption spectroscopy has been practiced for the crystals and compared with H_3BTC to provide additional proof for the incorporation of BTC^{3-} ligands in the framework (Figure S3). The carboxylic $\text{C}=\text{O}$ peak in Figure S3 is shifted from 1691 cm^{-1} of H_3BTC to 1616 cm^{-1} of compound **B2**, which supports the coordination of H_3BTC ligands to the cobalt (II) atoms. Powder X-ray diffraction pattern of the remnants of the crystals after thermogravimetric analysis (TGA) exactly matches that of cobalt oxide (Co_3O_4), proving that the incorporated metal is indeed cobalt (Figure S4). Moreover, the crystals of compound **B2** have been applied to various solvents including water, DMF, ethanol, and acetone, to further test its properties (Figure S5). The crystals remained stable under all solvents, except for water, in which a framework change was observed along with immediate color change to pink (Figure S6). The SEM image confirmed the complete change in framework structure of compound **B2** upon treatment with water (Figure S7). Additionally, powder X-ray diffraction pattern of the crystals after application of water has been compared with that of the prior state, which was discovered to be considerably different and strongly supported the change of framework in compound **B2** under water (Figure S8). To trace the direct cause of the framework change, energy dispersive spectroscopy has been performed for the crystals treated with water and the nitrogen atoms was revealed to be absent after addition of water. Since the nitrogen atoms are only included in the [BMI] cations, the

framework change has been suggested to be accompanied by the evacuation of [BMI] guest molecules (Figure S9). Conceding further research taken, presumably along with the relative stability observed under other common solvents, this phenomenon, the evacuation of cation molecules out of the framework structure, may open a possibility for the ionothermal methodology in preparing coordination polymers with a cation exchange property. Lastly, thermogravimetric analysis (TGA) of compound **B2** has confirmed the framework stable up to 352°C as shown in Figure S4(a), raising the potential of the compound for industrial applications.

4. Conclusions

We have reported a novel coordination polymer $[\text{BMI}]_2[\text{Co}_2(\text{BTC})_2(\text{H}_2\text{O})_2]$ (compound **B2**) and compared it within the system of polymers arising from ionothermal reaction of $\text{Co}(\text{OAc})_2$ and BTC mediated by the ionic solvent [RMI]Br. Resident inside the cavities, the cations have been expected to directly relate their sizes to the volume of the cavities. However, the accuracy of this assumption was curtailed by structural analysis of compound **B2** along with the discovery of significant bending in the alkyl chain of the BMI cations. Moreover, thermal stability and removability of the incorporated cations exhibited by compound **B2** further open the feasibility of implementing the ionothermal methodology for production of new materials with demanded properties.

Conflicts of Interest

There are no conflicts of interest regarding the publication of this paper.

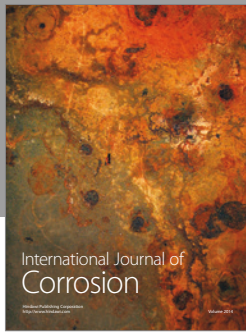
Acknowledgments

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