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# Mixed-Metal Imidazolates Containing Alkali and Alkaline Earth Metals: Mechanochemical Synthesis and Crystal Structure of $AMgIm_3$ (A = Na or K)

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Supporting Information

ABSTRACT: The first bimetallic imidazolates containing alkali and alkaline earth metals, NaMgIm<sub>3</sub> and KMgIm<sub>3</sub>, respectively, are prepared by mechanochemical synthesis and are reported in this paper. NaMgIm<sub>3</sub> has been prepared by the reaction between NaIm and  $Mg(BH_4)_2$  as well as directly from NaIm and MgIm<sub>2</sub>. Structural evolution and thermal stability were followed by an in situ high-temperature X-ray powder diffraction experiment utilizing synchrotron radiation. In both compounds, the imidazolate ligand is connected to four metal cations forming a complex three-dimensional network with channels running along the c-direction. NaMgIm<sub>3</sub> and KMgIm<sub>3</sub> are the first members of a new family of imidazolate frameworks with stp topology. The formation of mixed-alkali-



metal imidazolate compounds is thermodynamically controlled. LiIm and MgIm<sub>2</sub> have not yielded a mixed-metal compound, while KIm reacts swiftly and forms KMgIm<sub>3</sub>.

# INTRODUCTION

Materials research over the past several decades has been focused on providing novel platforms that could enable effective solutions for the world's growing demand for energy, where hydrogen is set as a key element within the quest for sustainable alternatives.<sup>1</sup> Different crystalline and/or porous systems have been considered as materials of choice for hydrogen storage, among which metal borohydrides, exhibiting a high gravimetric and volumetric hydrogen density, represent a very promising class of compounds where hydrogen is covalently bonded to a light element, forming complex BH<sub>4</sub> anions. A comprehensive review of the structural versatility and storage properties of different mono-, bi-, and trimetallic borohydrides is given in ref 2. The tetrahedral  $BH_4^-$  anion is a directional bridging ligand, coordinating metal cations preferably via its edges, as evidenced in the case of porous  $\gamma$ - $Mg(BH_4)_2$ .<sup>3</sup> Additionally, metal-organic frameworks (MOFs) and a subclass, zeolitic imidazolate frameworks (ZIFs), have also been most extensively studied as media in which hydrogen can be physisorbed in molecular form within the nanopores.<sup>4,5</sup> Although some MOFs are known to possess high hydrogen storage capacities, those are usually achieved only under extreme conditions such as low temperatures (77 K) as in case of MOF-505.6

The initial intention of our research was to explore the possibility of a coalescence between the class of borohydrides and imidazolates, which would result in the formation of coordination frameworks involving complex hydride anions as ligands. Coordinatively active anions, imidazolates, would serve as a structural unit of the framework, while borohydride anions could provide functionality. Imidazolates can act as bridging anionic ligands, thus allowing various connectivity and structural topologies of the resulting frameworks. Moreover, the feasibility of this idea relies upon the fact that a metalimidazole-metal bond angle of 145° is very similar to the observed metal-borohydride-metal angle, for example, in  $Mg(BH_4)_2$ . The proof of concept can be illustrated by the synthesis of the first mixed anion borohydride imidazolate, Li<sub>2</sub>ImBH<sub>4</sub>.<sup>8</sup> However, contrary to our expectation, the mechanochemical reaction between Mg(BH<sub>4</sub>)<sub>2</sub> and NaIm has not yielded a hybrid material containing both directional ligands but resulted in the formation of a new type of bimetallic imidazolate, NaMgIm<sub>3</sub>. Although imidazolates have rich and versatile coordination potential, especially highlighted in refs 9 and 10, bimetallic imidazolates are extremely scarce in

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the literature. Among the few known, the two-dimensional (2D) grid-shaped coordination polymer  $[Co^{II}Cu_2^I(Im)_4]$  has been reported.<sup>11</sup> The asymmetric unit contains a tetrahedrally coordinated cobalt(II) atom and a linearly coordinated copper(I) ion where metal centers are bridged by a deprotonated imidazole molecule. An interesting structure has been revealed for Cu<sub>2</sub>ZnIm<sub>6</sub>, exhibiting a network of alternating zinc and copper atoms bridged by imidazolate moieties, with the copper and zinc atoms surrounded by two and four imidazolate nitrogen atoms, respectively.<sup>12</sup> It is notable that the Cu(I)-Im-Zn(II) bridge found in this compound is analogous to those found in copper-zinc superoxide dismutase metalloenzymes.<sup>13</sup> Furthermore, recently, it has been demonstrated that zeolitic imidazolate frameworks are not restricted to exclusively tetrahedral nets, as in the first example of an imidazolate based on a bimetallic coordination net,  $In_2Zn_3(Im)_{12}$ , with In(III) in an octahedral coordination environment.<sup>9</sup> This structure has the topology of the Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> part of a garnet and provides an illustration of an extraordinarily rich chemistry awaiting systematic exploration of imidazolates. Nice example in which bimetallic imidazolate shows great dynamic uptake selectivity for CO<sub>2</sub> over methane under wet conditions is reported in ref 14. While those few examples of bimetallic imidazolates can be found in the literature in the case of transition-metal atoms, there are no reports of mixed-metal imidazolates involving alkali and earth alkali metals. It is shown that alkali imidazolates (NaIm, KIm, and LiIm) form the dense and hypercoordinated structures in which the coordinative demand of the metal cation increases with an increase in ionic radius. The Li<sup>+</sup> cation exhibits a strong propensity to form heteroleptic structures, while the K<sup>+</sup> cation coordinates the Im ring through the  $\pi$ -system.<sup>15</sup> On the other hand, the utilization of an alkali earth metal led to the formation of a porous zeolitic imidazolate framework in the case of magnesium imidazolate (MgIm<sub>2</sub>).<sup>15,16</sup> To the best of our knowledge, only transition metals were used as metal centers in bimetallic imidazolates, and this is the first time bimetallic imidazolates contain both alkali and alkaline earth metals.

#### EXPERIMENTAL SECTION

**Synthesis.** Four mechanochemical reactions between  $Mg(BH_4)_2$  or  $MgIm_2$  and AIm (A = Na, K, or Li) were conducted using the Planetary Micro Mill Fritsch Pulverisette 7 premium line. The reactants and stainless steel balls (d = 5 mm; m = 0.5 g) were loaded in a stainless steel vial (25 mL) under inert conditions. In each synthesis, the ball:sample mass ratio amounted to 25:1. Ball milling was performed at 550 rpm for 10 min, followed by a 5 min rest time; this procedure was repeated 12 times. The reactants and molar ratios used are listed in Table 1.

#### Table 1. Reactants Used for Mechanochemical Synthesis

S1	1:6 Mg(BH <sub>4</sub> ) <sub>2</sub> :NaIm
S2	1:1 MgIm <sub>2</sub> :NaIm
S3	1:1 MgIm <sub>2</sub> :KIm
S4	1:1 MgIm <sub>2</sub> :LiIm

Anhydrous magnesium borohydride,  $Mg(BH_4)_2$  (99.99%), was purchased from Sigma-Aldrich, while the imidazolates were prepared by the procedure reported elsewhere.<sup>15</sup> All handling and manipulation of the chemicals were performed in an argon-filled glovebox.

X-ray Powder Diffraction (XRPD) at Room Temperature (RT). XRPD measurements at RT were performed using a Stoe IPDS-P diffractometer with monochromated Cu K $\alpha$ 1 radiation ( $\lambda$  =

1.54060 Å) and a curved image plate detector, in Debye–Scherrer geometry. Air-sensitive samples were mounted in a glovebox in 0.8 mm borosilicate capillaries sealed with vacuum grease. Data were collected at RT, in the  $2\theta$  range of 2–100° with a counting time of 40 s/step. XRPD patterns are shown in Figures S1–S4.

Synchrotron Radiation X-ray Powder Diffraction (SR-XRPD) at High Temperature (HT). High-temperature *in situ* powder diffraction (HT-XRPD) data were collected at beamline BM01, SNBL at the ESRF, Grenoble, France. The samples were mounted in 0.5 mm borosilicate capillaries and closed with vacuum grease. The following measurement parameters were used:  $\lambda_{S1} = 0.8187$  Å,  $\lambda_{S2,S3,S4} = 0.7149$ Å, sample rotation of 0–40°, and X-ray exposure time of 40 s. The Dectris Pilatus 2M detector was used for recording 2D powder data at sample–detector distances of 200 or 400 mm. Samples were heated in the temperature range from RT to 400 °C (with a heating rate of 5 °C/min) by a heat blower. 2D images were integrated and treated with the local program Bubble.<sup>17</sup>

**Structure Solution, Analysis and Validation.** Crystal structures of new compounds were determined and refined from the SR-PXD data. Indexing, space group determination, and structure determination were carried out using the FOX program.<sup>18</sup> The structural model was refined by the Rietveld method using the Fullprof program.<sup>19</sup> The imidazolate anion was treated as a rigid body, and only its position and orientation in the unit cell were varied.

The topology analysis of the underlying net in the novel crystal structures was performed with the help of the program TOPOS.  $^{20}$ 

Bond valence sum (BVS) calculations are used for validation of the obtained structural models. Crystallographic positions, as determined by XRPD, were used for BVS calculation. Soft bond valence parameters  $R_{ij}$  and *b* were taken from ref 21. Results calculated from the most commonly adopted empirical expression for the variation of the length  $d_{ij}$  of a bond with valence  $v_{ij} = \exp[(R_{ij} - d_{ij})/b)$ , were summed to obtain the sum of all of the valences from a given atom.

The program VESTA was used for visualization of crystal structures.  $^{\rm 22}$ 

#### RESULTS AND DISCUSSION

Phase Analysis Using HT SR-XRPD Data. Diffraction patterns of as-milled products obtained after the mechanochemical reaction between  $Mg(BH_4)_2$  and NaIm, as well as in situ high-temperature data, are shown in Figure 1a. The onset crystallization temperatures (as well as the temperature when each phase disappears) will be discussed below, as determined from Figures 1a, 2a, and 3a. Figures 1b, 2b, and 3b show a representative pattern for each of the phases within the discussed temperature range. One can see that as-milled sample S1 contains unreacted NaIm and a significant amount of the amorphous phase(s). At 118 °C, a new crystalline phase, NaMgIm<sub>3</sub>, starts to appear (Figure 1b). With further thermal treatment, the diffraction lines of NaIm disappear at 209 °C. Simultaneously, another unknown crystalline phase starts to crystallize. As this unknown phase coexists together with NaMgIm<sub>3</sub>, the significant overlap of diffraction peaks prevented its successful structure determination. Moreover, this compound is stable in a very narrow temperature range, from 209 to 218 °C. However, additional experiments were conducted, and it was found that the new phase corresponds to a high-temperature polymorph of NaIm (HT-NaIm).<sup>23</sup> Above 218 °C, only NaMgIm<sub>3</sub> diffraction peaks are present. The compound remains stable up to 340 °C.

Additional mechanochemical synthesis was conducted, starting from  $MgIm_2$  and NaIm, to prepare pure  $NaMgIm_3$  and to gain further insight into its structural evolution and thermal stability. Diffraction patterns of as-milled products



Figure 1. (a) T ramp of sample S1. (b) Phase analysis of sample S1 with a T ramp. Diffraction lines of NaIm are denoted with diamonds. The NaMgIm<sub>3</sub> phase is denoted with circles. The HT-NaIm phase is denoted with times signs.



**Figure 2.** (a) *T* ramp of sample S2. (b) Phase analysis of sample S2 with a *T* ramp. Diffraction lines belonging to the NaMgIm<sub>3</sub> phase are denoted with circles, and the diffraction lines belonging to the MgIm<sub>2</sub> phase with squares.



Figure 3. (a) T ramp of sample S3. (b) Phase analysis of sample S3 with a T ramp. Ladders denote the diffraction lines of the KMgIm<sub>3</sub> phase.

obtained after the mechanochemical reaction as well as *in situ* high-temperature data are shown in Figure 2.

As one can see from Figure 2, as-milled sample S2 is amorphous up to 149 °C when NaMgIm<sub>3</sub> starts to crystallize.

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**Figure 4.** Phase analysis of the Li sample with a T ramp. Squares denote the diffraction lines of the MgIm<sub>2</sub> phase, and asterisks denote the diffraction lines of the LiIm phase.

It remains stable up to 310 °C. At 310 °C, the diffraction lines of NaMgIm<sub>3</sub> disappear and MgIm<sub>2</sub> starts to crystallize. Magnesium imidazolate was stable up to 366 °C. Interestingly, one can notice that NaMgIm<sub>3</sub> displays a wider range of thermal stability (118–340 °C) when borohydride is present in the system.

Because the mechanochemical reaction between  $MgIm_2$  and NaIm yielded a novel bimetallic imidazolate compound, further attempts have been made to prepare novel mixedmetal imidazolates containing K and Li instead of Na.

Table 2. Cryst	tal Data and a	a Summary	of Structure
Refinement D	ata for NaMg	Im <sub>3</sub> and KI	MgIm <sub>3</sub>

	$NaMgIm_3$	KMgIm <sub>3</sub>
profile function	pseudo-Voigt	pseudo-Voigt
R (profile) (%)	16.9	11.8
R (weighted profile) (%)	10.7	10.9
$\chi^2$	$7.01 \times 10^{3}$	$8.03 \times 10^{4}$
space group	P6 <sub>3</sub> 22	P6322
a (Å)	9.5053(4)	9.22628(15)
c (Å)	6.57606(15)	7.50903(13)

Diffraction patterns of as-milled products obtained after the mechanochemical reaction between  $MgIm_2$  and KIm (S3) as well as *in situ* high-temperature measurements are shown in Figure 3.

In the case of KIm, unlike that of NaIm, the grinding without any thermal treatment proved to be sufficient for the formation of the mixed-metal imidazolate phase, KMgIm<sub>3</sub>. This compound is stable in a wide temperature range, from RT to 353 °C, when it melts. The same compound recrystallizes below 298 °C during cooling. The crystal structure of KMgIm<sub>3</sub> has also been determined from powder X-ray diffraction data.

When LiIm was used as a reactant in mechanochemical reaction with  $MgIm_2$ , the milled sample at RT shows only an amorphous halo (Figure 4). Diffraction lines of LiIm start to appear at 149 °C, and the second reactant,  $MgIm_2$ , starts to crystallize at 185 °C. Both compounds remained stable up to



**Figure 5.** (a) Rietveld refinement of NaMgIm<sub>3</sub>. The experimental pattern is given as red dots; the black curve shows the calculated profile, and the difference curve is colored blue. Vertical marks represent Bragg reflections of NaMgIm<sub>3</sub>. (b) Crystal structure of NaMgIm<sub>3</sub>. Magnesium atoms are shown as purple spheres. Sodium is colored yellow, carbon gray, and nitrogen blue. (c) Extended crystal packing of NaMgIm<sub>3</sub> showing channels along the *c*-direction.



Figure 6. (a) Rietveld refinement of KMgIm<sub>3</sub>. The experimental pattern is given as red dots; the black curve shows the calculated profile, and the difference curve is colored blue. Vertical marks represent Bragg reflections of NaMgIm<sub>3</sub>. (b) Crystal structure of KMgIm<sub>3</sub>. Magnesium atoms are shown as purple spheres. Potassium is colored violet, carbon gray, and nitrogen blue. (c) Extended crystal packing of NaMgIm<sub>3</sub> showing channels along the *c*-direction.

296 °C. No formation of a mixed-metal imidazolate was observed.

**Crystal Structure of AMgIm<sub>3</sub> (A = Na or K).** The crystal structure of NaMgIm<sub>3</sub> was determineed using the diffraction data of sample S1 at 262 °C and of sample S3 at 333 °C. The selected diffraction peaks were indexed in a hexagonal cell. For structure determination, positions of one Na atom, one Mg atom, and one imidazolate group for NaMgIm<sub>3</sub> and positions of one K atom, one Mg atom, and one imidazolate group for KMgIm<sub>3</sub> were varied using corresponding antibump restraints. A Rietveld plot from the refinement of NaMgIm<sub>3</sub> is given in Figure 5a, and the crystal structure is shown in panels b and c of Figure 5. The compound crystallizes in a hexagonal system (space group  $P6_322$ ). Crystal data for NaMgIm<sub>3</sub> and a summary of structure refinement data are listed in Table 2.

Unlike monometallic imidazolates (NaIm and MgIm<sub>2</sub>) that show tetrahedral coordination of metals,<sup>14</sup> in NaMgIm<sub>3</sub> both Na and Mg cations exhibit distorted octahedral coordination. The interatomic distances,  $d(M-N_{im})$ , are found to be longer in the case of mixed-metal imidazolates, as expected for a higher coordination number, compared to those of tetrahedrally coordinated metal cations in the case of NaIm and MgIm<sub>2</sub> [ $d(Na-N)_{tet} = 2.4029$  Å, and  $d(Na-N)_{oct} = 2.5851$  Å;  $d(Mg-N)_{tet} = 2.0410$  Å, and  $d(Mg-N)_{oct} = 2.3701$  Å]. As in NaIm, the imidazolate ligand is connected to four metal cations, where each N atom from the imidazolate anion is coordinated with two cations forming a complex threedimensional network. Along the *c*-direction, Na and Mg are connected via bridging N atoms from three imidazole rings forming the chain of face-shared metal octahedra. Those chains along the *c*-direction are mutually connected in an imidazolebridged fashion, forming a zigzag net in the a-b plane. A crystal packing view also reveals channels running along the *c*direction, located on the 6-fold screw axis, as shown in Figure 5c. The channel is defined by a diameter *d* of ~6.6 Å, and the empty volume calculated from the contact surface amounts to 28.5 Å<sup>3</sup> (assuming a spherical probe of r = 1.4 Å).

It was found that the crystal structure of KMgIm<sub>3</sub> is similar to that of its sodium derivative (Figure 6b). Rietveld refinement is shown in Figure 6a. Crystal data for both NaMgIm<sub>3</sub> and KMgIm<sub>3</sub>, together with a summary of structure refinement, are listed in Table 2.

The main difference between crystal structures of NaMgIm<sub>3</sub> and KMgIm<sub>3</sub> is related to the orientation of the imidazolate rings. Although the imidazolate rings in the case of the sodium compound deviate slightly from an ideal planar configuration, the rings can be considered as almost parallel to the *a*-*b* plane, which is not the case for the potassium compound. Additionally, the two compounds show different degrees of polyhedral deformation around the alkali-metal cation; a pronounced distortion of octahedra around sodium can be observed  $[\angle(N_{ax}-Na-N_{eq}) = 76.65^{\circ}]$ , compared to the octahedra surrounding the potassium center  $[\angle(N_{ax}-K-N_{eq}) = 84.45^{\circ}]$ .

According to BVS calculations, in NaMgIm<sub>3</sub>, the valence sums for magnesium and sodium cations amount to 1.5 and 1, respectively. In the case of KMgIm<sub>3</sub>, the valence sums for magnesium and potassium are 1.6 and 0.65, respectively. The calculated values are lower than expected because the tables of calculated  $R_{ij}$  values correspond to an isolated N<sup>3-</sup> anion.

The topology analysis of NaMgIm<sub>3</sub> has found that the underlying net is of the stp type. There are few MOFs with this topology type in the CSD database and few inorganic compounds in the ICSD database. They all have a common structure type belonging to iron phosphonate  $Fe_2(HPO_3)_3$ . It is not a structural prototype of NaMgIm<sub>3</sub>, because the anion is different (phosphonate instead of imidazolate), and therefore, the space group is  $P6_3/m$  instead of  $P6_322$ . One more difference between NaMgIm<sub>3</sub> and Fe phosphonate is that in the latter two octahedral nodes are occupied by the same atom type (Fe).

# CONCLUSION

In conclusion, it appears that the formation of AMgIm<sub>3</sub> compounds, where A is Li, Na, or K, is governed by the thermodynamic stability of the alkali-metal imidazolates versus the energy of formation of mixed-metal imidazolate compounds; while lithium imidazolate does not react with magnesium imidazolate likely due to the limitation imposed by a small Li cation (A cations in AMgIm<sub>3</sub> have a coordination number 6), potassium imidazolate swiftly reacts with MgIm<sub>2</sub> and forms KMgIm<sub>3</sub>. The double-cation imidazolates of magnesium and sodium or potassium are the first members of new family of imidazolate frameworks with stp topology.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00446.

PXRD data of sample S1 (Figure S1), PXRD data of sample S2, as prepared and thermally treated at 220 °C (Figure S2), PXRD data of sample S3 (Figure S3), and PXRD data of the Li sample (Figure S4) (PDF)

#### Accession Codes

CCDC 1896592–1896593 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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