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An Intermediate for the Clean Synthesis of Ionic Liquids: Isolation and Crystal Structure of 1,3-Dimethylimidazolium Hydrogen Carbonate Monohydrate

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Abstract: 1,3-Dimethylimidazolium-2-carboxylate and carbonic acid have been used to prepare a 1,3-dimethylimidazolium hydrogen carbonate salt by means of a Krapcho reaction. The ability to form hydrogen carbonate azolium salts allows for them to be used as precursors for fast, efficient, environmentally benign, and halide-free syntheses of many ionic liquids by a simple, acid–base reaction of virtually any acid (inorganic, organic, and organic noncarboxylic) with a pK_a less than that of HCO_3^-. Additionally, the kinetics of this reaction can be accelerated by employing catalytic amounts of DMSO (a traditional Krapcho solvent used in decarboxylation reactions) to catalyze the decarboxylation. The crystal structure of 1,3-dimethylimidazolium hydrogen carbonate monohydrate is the first example of an imidazolium-based hydrogen carbonate salt. There is a strong 2D hydrogen-bonded network with facially π-stacked imidazolium cations located in the cavities created by this framework.

Keywords: halide-free syntheses · imidazolium salts · ionic liquids · Krapcho reaction · X-ray diffraction

Introduction

Currently the most common synthetic routes for ionic liquids (ILs) involve metathesis reactions from halide intermediates, by an inorganic halide precipitation or liquid/liquid separation, to the desired products.[1] Though this procedure is simple, complete removal of the halide is time-consuming, costly, and leads to depressed yields, attributable to inherent loss of the IL during the purification process. In some applications, halide contamination is acceptable, but for others, even ppm quantities of chloride can poison expensive catalysts, rendering them useless.[2] Current approaches circumventing halide contaminants include halide-free syntheses of imidazolium-based ILs by using dialkylsulfate[3,4] or dimethylcarbonate (DMC) methylating agents, and these have provided efficient routes.[5,6]

Additionally, our group has recently investigated the utilization of 1,3-dimethylimidazolium-2-carboxylate (1,3-diMIM-2-(COO)),[6] focusing on the carboxylate functionality appended to the C2 carbon atom of an azolium core as a gateway to halide-free syntheses for both hydrophobic and hydrophilic ILs by decarboxylation of the carboxylate with strong protic acids (for example, HPF_6, HBF_4, picric acid, and H_2SO_4).[7] It was noted that the strength of the protic acid affects the decarboxylation of 1,3-diMIM-2-(COO); the lower the pK_a of the acid, the faster it reacts, forming 1,3-dimethylimidazolium ([1,3-diMIM]$^+$)-based ILs. In the case of HNO_3, the primary product formed in the reaction was the protonated salt of the starting material, 2-carboxy-1,3-dimethylimidazolium nitrate ([2-(COOH)-1,3-diMIM][NO_3]) which is stable at room temperature. The decarboxylation of [2-(COOH)-1,3-diMIM][NO_3] was achieved by either heating the sample or chemically by the addition of DMSO, which catalyzes decarboxylation through a Krapcho mechanism. From these observations, it was determined that strong acids will cause decarboxylation, leading to the product without the need for heating or addition of catalytic amounts of a traditional Krapcho reaction solvent.[7]

In the past few years it has been recognized that to achieve the goal of ultra-pure ILs, the effort can no longer be focused on improvement of currently used purification techniques, rather, focus should be on the design of synthetic routes for the formation of ILs in processes that assure contaminant-free products. Thus, highly desirable, clean, contaminant-free intermediates for a variety of ILs could come from a class of anions which can easily be used by further metathesis reactions, leaving no byproducts or original

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anion, even in trace amounts. One approach is to have a reactive precursor to the desired anion which could form the desired product and inert byproduct(s). The carbonate anion would be an ideal candidate as it cleanly decomposes to gaseous CO_2 and H_2O in the presence of stronger acids.

The ability to synthesize a stable $[HCO_3]^-$-based IL would thus allow the synthesis of an intermediate for the formation of virtually any IL by simple reaction of this precursor with any protic acid stronger than HCO_3^- (pK_{a1} (H_2CO_3) 6.352).[8] Due to the limited stability of H_2CO_3 formed in the reaction and its fast decomposition, utilization of this synthetic protocol would allow for the formation of halide and metal-free ILs, with the only byproducts being H_2O and gaseous CO_2. Additionally, the evacuation of gaseous byproducts would greatly contribute to the process as an additional driving force for the reaction.

It should also be pointed out that the reaction of $[HCO_3]^-$ with protic acids and the decomposition of H_2CO_3 is not limited to acids with p$K_a < 6.35$ due to the associated speciation of the carbonate anion. Under ambient conditions at a pH of 7.25, 10% of all carbonate present in the system still exists as H_2CO_3. Thus, in the presence of excess protons from an acid source, an increase in the concentration of H_2CO_3 occurs, and thermodynamic decomposition of H_2CO_3 is favored.[9] This decomposition process might not be kinetically fast with weaker protic acids, but heating or reduction of pressure would increase the kinetics.

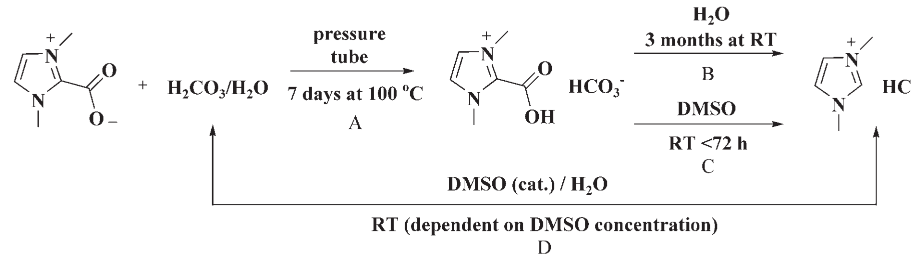
Even though the synthesis of a $[CO_3]^{2-}$-based imidazolium salt might seem to be even more attractive over the formation of $[HCO_3]^-$-based salts, the formation of a CO_3^{2-} salt (pK_{a2} (HCO_3^-) 10.329)[8] would still not allow for metathesis with weaker protic acids than those of a $[HCO_3]^-$-based salt (as CO_3^{2-} must first undergo a protonation reaction to form HCO_3^- anyway) and thus would not extend the potential product scope. Additionally, the formation of the more basic CO_3^{2-} anion would only decrease the stability of the imidazolium cation, as a result of its mildly acidic C2 proton, which could react leaving an unstable or reactive imidazylidene. Recently, for example, this route for carbene formation has been exploited in the synthesis of 2-carboxylate azolium zwitterions.[10]

Recent patent literature has proposed high temperature, high pressure reaction conditions to initially form imidazolium-based (but not limited to the azolium-based cation) formate salts, which are oxidized with H_2O_2/Pd to the desired carbonate anion.[11,12] Additionally, DMC has also been shown to yield tetramethylammonium carbonates with ILs being employed as catalysts, but with very depressed yields.[13] Previous patent literature[14] has proposed the usefulness of a $[HCO_3]^-$-based IL for the halide-free synthesis of many other ILs through titration with a Brønsted acid and has recently been scaled-up according to the most recent Sigma–Aldrich catalog.[15]

Here, we demonstrate the use of a stable, yet reactive, azolium-based zwitterion, 1,3-diMIM-2-(COO), and H_2CO_3 in the synthesis of a novel 1,3-dimethylimidazolium hydrogen carbonate ([1,3-diMIM][HCO_3]) salt. The synthesis proceeds by means of a Krapcho reaction in which HCO_3^- serves as a weak nucleophile and water as the polar solvent in the decarboxylation of 2-carboxy-1,3-dimethylimidazolium hydrogen carbonate ([2-(COOH)-1,3-diMIM][HCO_3]), resulting in [1,3-diMIM][HCO_3]. We have also found that the synthesis can be completed in one step by protonation/decarboxylation in the presence of DMSO in deionized water, with CO_2 absorbed from the atmosphere or purged through the system. The kinetics of the reaction can be increased by increasing the concentration of H_2CO_3 in the system, which can be achieved by increasing the pressure of CO_2.

Results and Discussion

It was expected that spontaneous decarboxylation would not occur when 1,3-diMIM-2-(COO) and H_2CO_3 were reacted even at an elevated temperature and pressure.[7] H_2CO_3 was thought to be too weak of an acid to lead to decarboxylation, thus, the reaction was expected to proceed from 1,3-diMIM-2-(COO) to [2-(COOH)-1,3-diMIM][HCO_3], which then could undergo the solvent-supported decarboxylation by using a traditional Krapcho solvent (polar aprotic solvent, for example, DMSO), yielding [1,3-diMIM][HCO_3], Scheme 1. This hypothesis was based on the assumption that traditionally, Krapcho decarboxylation reactions require: 1) a strong nucleophile and 2) a polar aprotic solvent.[16,17] Surprisingly, over time, [2-(COOH)-1,3-diMIM][HCO_3] decarboxylated through a Krapcho reaction in the presence of only HCO_3^- and water (Scheme 1, path B). Spontaneous decarboxylation has not been observed in previous Krapcho reactions with such a weak nucleophile (for example,

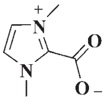
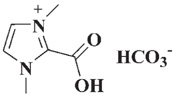
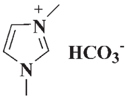


Scheme 1. Synthetic routes to [1,3-diMIM][HCO_3] from 1,3-diMIM-2-(COO).

HCO_3^-) and a polar protic solvent (for example, H_2O). Parallel to this finding, we also confirmed that the decarboxylation of [2-(COOH)-1,3-diMIM][HCO_3] does occur under traditional Krapcho conditions, with the use of DMSO (Scheme 1, path C).

NMR spectroscopic characterization of all three imidazolium species (with the carboxylate-terminus on C2, on the starting material, 1,3-diMIM-2-(COO), the intermediate [2-(COOH)-1,3-diMIM][HCO_3], and the decarboxylated product [1,3-diMIM][HCO_3]) is especially difficult due to very small changes in the electron density around the C2 carbon atom in the imidazolium cores. To correctly analyze and distinguish between the compounds, an in depth analysis of all three with both ^1H and ^{13}C NMR spectra are needed (Table 1).

Table 1. Comparison of ^1H and ^{13}C NMR shifts in [D_6]DMSO.

		Me	C4/C5	C2	C(O_2)	C(O_2)H	HCO_3
 [1,3-diMIM-2-(COO)]	^1H	3.96	7.52	–	–	–	–
	^{13}C	36.5	123.5	141.0	157.1	–	–
 [2-(COOH)-1,3-diMIM][HCO_3]	^1H	3.91	7.58	–	–	–	≈9.4
	^{13}C	36.2	124.5	138.4	–	≈154	160.6
 [1,3-diMIM][HCO_3]	^1H	3.84	7.59	8.04	–	–	≈9.4
	^{13}C	36.4	123.2	137.6	–	–	159.0

We have also found that when [1,3-diMIM][HCO_3] is dissolved in methanol, an unexpected, slow reaction occurs between the solvent and the product with the formation of 1,3-dimethylimidazolium methylcarbonate ([1,3-diMIM]-[$MeCO_3$]) and H_2O (confirmed by NMR spectroscopy). This reaction is driven forward through the formation of a weaker acid, methylcarbonate, but nonetheless, in the presence of a protic acid with a pK_a less than that of $MeCO_3^-$, metathesis can still occur, leaving only methanol, H_2O, and CO_2.

Dissolution of 1,3-diMIM-2-(COO) in [D_6]DMSO with variable concentrations of H_2O, in which H_2CO_3 is also present, revealed an unknown set of peaks with variable ratios to the starting material. Further investigation showed that the ratio of the unknown peaks had a kinetic and water concentration dependency in the NMR spectra (Scheme 1, path D). As the concentration of water increases, more 1,3-diMIM-2-(COO) reacts to form [1,3-diMIM][HCO_3], by the Krapcho decarboxylation reaction (Figure 1).

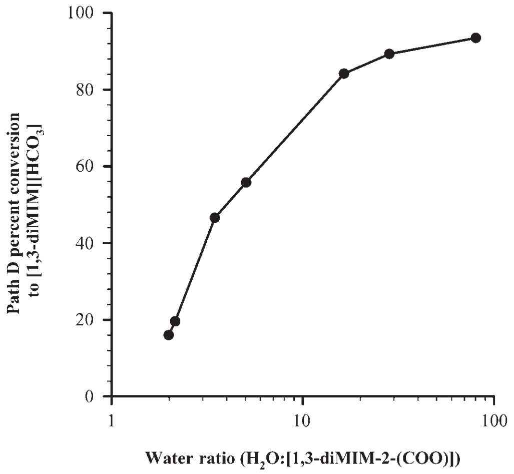


Figure 1. Reaction scheme, path D, 1,3-diMIM-2-(COO) to [1,3-diMIM]-[HCO_3] as a function of water ratio.

From a stock solution of 1,3-diMIM-2-(COO) in [D_6]DMSO, equal amounts were added to fresh glass vials in which additional [D_6]DMSO and H_2O (polished to 18.1–18.2 MΩcm, then saturated with atmospheric CO_2 before use) were added at variable ratios with the total volume kept constant at 1 mL. All samples where capped and allowed to sit for 72 h at room temperature before being transferred to NMR tubes for ^1H NMR spectroscopic analysis. The water:1,3-diMIM-2-(COO) ratio was determined by peak integrations from the NMR spectra (Figure 1).

The results can be explained as follows: 1) the more water present, the higher the ratio of H_2CO_3 to imidazolium salt; 2) DMSO causes decarboxylation of the protonated imidazolium salt; 3) in the presence of excess H_2O, the reaction is driven toward formation of the final product, thus when the water concentration is low, the starting material, 1,3-diMIM-2-(COO), is favored. Given enough time, complete decarboxylation of 1,3-diMIM-2-(COO) can occur, as long as H_2O, CO_2, and DMSO are present in the solution. We speculate that to further increase the kinetics of this reaction, and scale-up the process, pressurized CO_2 would increase the solubility of carbonate species in water, thus increasing the attainable concentration of H_2CO_3 in solution.

We have also noticed that the process described in Figure 1, path D is reversible if the solid sample is stored "dry" with trace amounts of DMSO, as the system is in equilibrium with the starting material, 1,3-diMIM-2-(COO). This was visually observed for the solid [1,3-diMIM]-[HCO_3]·nH_2O, for which over time, the solid converted back to the thermodynamically favored 1,3-diMIM-2-(COO) with the release of one mole of water which further solvated the sample. We speculate that, though kinetically slow, reverse carboxylation of the C2 carbon atom is thermodynamically favored due to formation of a fully conjugated, overall neutral, zwitterionic molecule (1,3-diMIM-2-(COO)) in comparison to the charge-separated organic salt ([1,3-diMIM][HCO_3]). This reverse reaction was monitored with ^1H and ^{13}C NMR spectroscopy.

Structural Characterization

Due to the small differences in the NMR spectra of the three imidazolium salts, definitive proof of the synthesis by NMR spectroscopy is problematic. The crystallographic characterization of the highly deliquescent, colorless, plate-like crystals of [1,3-diMIM][HCO_3]·H_2O isolated from the mother liquor provides the first structurally characterized imidazolium-based hydrogen carbonate salt. The asymmetric unit is provided in Figure 2 and consists of one cation, H_2O, and HCO_3^-. The HCO_3^- anions form hydrogen-bonded dimers around crystallographic centers of inversion.

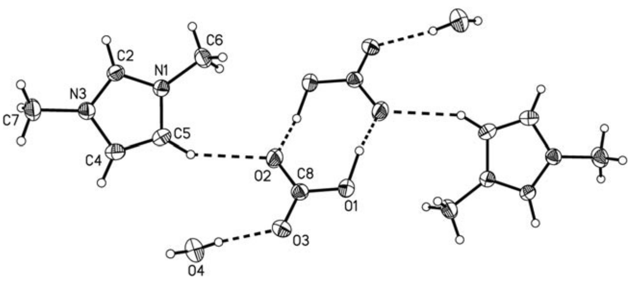


Figure 2. ORTEP illustration (50% probability thermal ellipsoids) of the [1,3-diMIM][HCO_3]·H_2O hydrogen-bonded dimer.

Hydrogen bonding about the anion is shown in Figure 3a, in which a total of eight significant interactions are observed. The hydrogen bound to O1 has a slightly elongated bond (1.19(4) Å) and is disordered, which is not unusual for carbonate dimers.[18–21] The remaining close contacts about the anion include: O4-H2O4···O3 = 1.97(2) Å, 171(2)°; C5-H5A···O2 = 2.38(2) Å, 151(1)°; O1-H1O1···O2 = 1.42(4) Å, 171(3)°; O4-H1O4···O3 = 2.02(2) Å, 166(2)°. Contacts around each cation (Figure 3b) include interactions with four different HCO_3^- dimers and one water molecule: C5-H5A···O2 = 2.38(2) Å, 151(1)°; C2-H2A···O1 = 2.40(2) Å, 153(1)°; C4-H4A···O3 = 2.41(2) Å, 148(2)°; C7-H7B···O3 = 2.47(3) Å, 167(2)°; and C6-H6A···O4 = 2.60(3) Å, 156(2)°.

It is, however, the hydrogen bonding between the anionic dimer and the water molecules which give rise to the interesting supramolecular features observed for this compound. Although this 2D anionic network has a unique topology, the H_2O–dimer interactions are similar to 1D chains observed in a previous structure, for which sets of HCO_3^- dimers, oriented in the same direction as the chain propagation, are connected via the terminal oxygen by two H_2O molecules, resulting in rows of chains separated by large hetero-organic molecules.[21] In the framework we report here, linear chains of H_2O···O3 are connected by HCO_3^- dimers (Figure 3c) to form 2D sheets. Water interacts with alternating rows of dimers to make up the framework yielding a brickwork pattern. Oppositely oriented pairs of π-stacked (3.53(3) Å) cations are locked within the voids of the brickwork-like hydrogen-bonded lattice (Figure 3d).

The incorporation of H_2O in these networks results in a bending of the sheets at the H_2O locations. Individually, these H_2O···HCO_3^- and HCO_3^-···HCO_3^- interactions are common,[21] but the combination of linear chains cross-linked by HCO_3^- dimers in this array has not previously been observed.

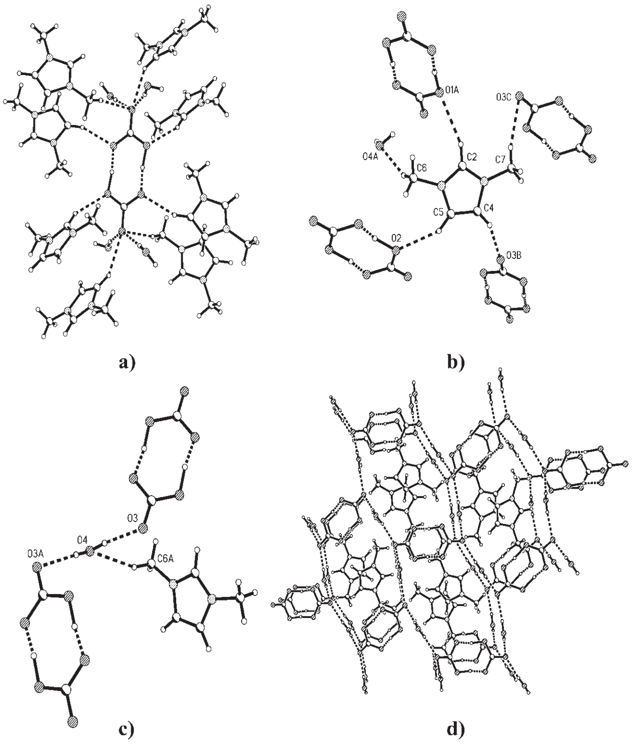


Figure 3. Supramolecular features of [1,3-diMIM][HCO_3]·H_2O: a) hydrogen bonding about each HCO_3^- dimer includes four water molecules and eight cations, b) close contacts around each cation, c) contacts around each water molecule, and d) the two-dimensional hydrogen-bonding network made up of 1D H_2O···**O3**···H_2O chains linked by HCO_3^- dimers in a brickwork lattice. Pairs of cations are π-stacked within the framework.

Conclusions

The chemistry of the carbonate anion in H_2O is closely tied to CO_2, pH, and pressure. Through the proper manipulation of these variables, the synthesis and subsequent isolation of the first azolium-based hydrogen carbonate salt was accomplished. Initially, this was achieved through the use of pressure and CO_2 (by increased H_2CO_3 concentrations in situ) to protonate 1,3-diMIM-2-(COO), followed by decarboxylation by means of a Krapcho reaction in an aqueous media. Next, we found that the kinetically slow decarboxylation reaction of [2-(COOH)-1,3-diMIM][HCO_3] can proceed in an aqueous environment, and that it can be accelerated by the addition of DMSO to yield [1,3-diMIM][HCO_3]. Furthermore, we have shown that the same product can be obtained when the reaction is carried out in an aqueous solution with addition of DMSO, naturally absorbed CO_2 from the atmosphere, and without added pressure.

Carbonate-based imidazolium salts not only promise a wide range of applications themselves, but also offer clean intermediates for halide-free syntheses of a large number of imidazolium-based ILs. The speciation of H_2CO_3 is pH dependent (at pH 7.25, 10% of the carbonate is present as H_2CO_3) and in the presence of a proton source from a stronger acid more of the HCO_3^- will be protonated forming H_2CO_3, thus promoting further decomposition of H_2CO_3 to CO_2 and H_2O. Thus, clean metathesis reactions providing a large number of new ILs are possible. Though these reactions would be kinetically slow, under mild heating and reduced pressure the titration of HCO_3^- with acid will still proceed to completion.

Experimental Section

DMC and 1-methylimidazole were purchased from Aldrich (Milwaukee, WI) and 1-methylimidazole was distilled prior to use. Synthesis of 1,3-diMIM-2-(COO) followed a previously published method, and purity was confirmed by means of ^1H and ^{13}C NMR spectroscopy.[4] Into a 10 mL thick-walled glass pressure tube, 1,3-diMIM-2-(COO) (0.5 g, 4.8 mmol) was added to room temperature carbonated water (7 mL, about 3% wt/wt H_2CO_3), purchased from Publix Super Market as Syfo brand seltzer water, and heated at 100°C for 7 days (Scheme 1, path A). The intermediate [2-(COOH)-1,3-diMIM][HCO_3] was dried by purging with dry air until the bulk water had been removed, followed by 24 h of drying in vacuo at room temperature, yielding an amorphous white solid. The sample was stored in a closed vial for 3 months at room temperature, during which time the sample absorbed atmospheric water and large colorless plate-like crystals grew by means of decarboxylation. The crystals were isolated and identified as [1,3-diMIM][HCO_3]·H_2O. The mother liquor contained solvated [2-(COOH)-1,3-diMIM][HCO_3] (confirmed by NMR spectroscopy) and became a thick liquid due to adsorbed atmospheric humidity (Scheme 1, path B).

In later studies, we found that [2-(COOH)-1,3-diMIM][HCO_3] can undergo decarboxylation in much shorter times with the addition of a Krapcho solvent (for example, DMSO) as previously reported.[6] The rate of decarboxylation is a function of the concentration of DMSO, but even with catalytic amounts of DMSO (10 µL in 5 mL of H_2O with ≈0.5 g of [2-(COOH)-1,3-diMIM][HCO_3]), complete decarboxylation occurs in less than 72 h (as monitored by ^1H NMR spectroscopy; Scheme 1, path C).

For larger-scale syntheses, path D (Scheme 1) allows for multigram quantities without the use of pressure or heat. In 50 mL of deionized H_2O (Nanopure, Barnstead, Dubuque, Iowa, 18.1–18.2 MΩcm), 3.9906 g of 1,3-diMIM-2-(COO) was dissolved and DMSO (10 µL) was added. The sample was allowed to sit for 3 weeks in an open beaker to allow absorption of CO_2 into the solution (forming H_2CO_3) before the water was evaporated. The sample was initially dried by purging air across the sample until a thick liquid was left. After transferring the liquid to a smaller vial, it was dried in vacuo at room temperature, yielding NMR pure [1,3-diMIM][HCO_3]·$n\,H_2O$ approaching quantitative yield.

1,3-Dimethylimidazolium-2-carboxylate (1,3-diMIM-2-(COO)): ^1H NMR (500 MHz, D_2O, 25°C): $\delta = 4.07$ (s, 6H; CH_3), 7.48 ppm (s, 2H; CH), ^{13}C NMR (126 MHz): $\delta = 37.04$ (CH_3), 123.30 (CH), 139.98 (C), 158.31 ppm ($C(O)_2$); ^1H NMR (500 MHz, [D_4]MeOH, 25°C): $\delta = 3.96$ (s, 6H; CH_3), 7.44 ppm (s, 2H; CH); ^{13}C NMR (126 MHz): $\delta = 37.55$ (CH_3), 123.52 (CH), 141.44 (C), 157.05 ppm ($C(O)_2$); ^1H NMR (500 MHz, [D_6]DMSO, 25°C): $\delta = 3.97$ (s, 6H; CH_3), 7.52 ppm (s, 2H; CH); ^{13}C NMR (126 MHz): $\delta = 36.47$ (CH_3), 123.52 (CH), 141.01 (C), 157.06 ppm ($C(O)_2$).

2-Carboxy-1,3-dimethylimidazolium hydrogen carbonate ([2-(COOH)-1,3-diMIM][HCO_3]): ^1H NMR (500 MHz, D_2O, 25°C): $\delta = 4.02$ (s, 6H; CH_3), 7.46 ppm (s, 2H; CH); ^{13}C NMR (126 MHz): $\delta = 38.14$ (CH_3), 124.43 (CH), 132.07 (C), 155.84 ($C(O)_2H$), 161.90 ppm (HCO_3^-); ^1H NMR (500 MHz, [D_4]MeOH, 25°C): $\delta = 4.09$ (s, 6H; CH_3), 7.48 ppm (s, 2H; CH); ^{13}C NMR (126 MHz) 37.99 (CH_3), 124.97 (CH), 142.60 (C), 153.43 ($C(O)_2H$), 158.00 ppm (HCO_3^-); ^1H NMR (500 MHz, [D_6]DMSO, 25°C): $\delta = 3.91$ (s, 6H; CH_3), 7.58 (s, 2H; CH), ≈9.40 ppm (b, 1H, HCO_3^-); ^{13}C NMR (126 MHz): $\delta = 36.18$ (CH_3), 124.54 (CH), 138.72 (C), ≈154 ($C(O)_2H$), 160.60 ppm (HCO_3^-).

1,3-Dimethylimidazolium hydrogen carbonate ([1,3-diMIM][HCO_3]): ^1H NMR (500 MHz, D_2O, 25°C): $\delta = 3.80$ (s, 6H; CH_3), 7.32 ppm (s, 2H; CH); ^{13}C NMR (126 MHz): $\delta = 38.57$ (CH_3), 123.00 (CH), 133.12 (C), 161.02 ppm (HCO_3^-); ^1H NMR (500 MHz, [D_4]MeOH, 25°C): $\delta = 3.86$ (s, 6H; CH_3), 7.51 (s, 2H; CH), 9.10 ppm (s, 1H; CH); ^{13}C NMR (126 MHz): $\delta = 36.47$ (CH_3), 124.18 (CH), 137.19 (C), 159.87 ppm (HCO_3^-); ^1H NMR (500 MHz, [D_6]DMSO, 25°C): $\delta = 3.84$ (s, 6H; CH_3), 7.58 (s, 2H; CH), 8.02 ppm (s, 1H; CH), ≈9.40 (b, 1H, HCO_3^-); ^{13}C NMR (126 MHz): $\delta = 36.40$ (CH_3), 123.21 (CH), 137.58 (C), 159.00 ppm (HCO_3^-).

1,3-Dimethylimidazolium methylcarbonate ([1,3-diMIM][$MeCO_3$]): ^1H NMR (500 MHz, [D_4]MeOH, 25°C): $\delta = 4.09$ (s, 6H; CH_3), 4.24 (s, 3H; CH_3), 7.75 (s, 2H; CH), 9.08 ppm (s, 1H; CH); ^{13}C NMR (126 MHz): $\delta = 36.49$ (CH_3), 39.52 ($\mathit{C}H_3CO_3^-$), 124.85 (CH), 138.44 (C), 160.96 ppm ($CH_3\mathit{C}O_3^-$).

Crystallographic data for [1,3-diMIM][HCO_3]·H_2O: Crystal size = 0.25 × 0.20 × 0.10 mm; monoclinic; space group = $P2_1/n$; $a = 7.2671(18)$, $b = 9.224(2)$, $c = 12.750(3)$ Å; $\beta = 98.350(5)°$; $V = 845.6(4)$ Å^3; $\rho_{calcd} = 1.384$ Mg m^{-3}; $2\theta_{max} = 56.62°$; $Mo_{K\alpha}$ radiation (graphite monochromated) $\lambda = 0.71073$ Å; ω scans; $T = 173(2)$ K; reflections: measured = 6034, independent = 2011, 6026 reflections included in refinement, GOF = 1.094 treated for absorption by using SADABS[22] (μ (mm^{-1}) = 0.116, min/max transmission = 0.868791); structure solution by using SHELXS, structure refinement with SHELXTL;[23] 157 parameters; hydrogen atoms were located from a difference Fourier map and refined isotropically; R_1, wR_2 $[I > 2\sigma(I)] = 0.0401$, 0.1022, R_1, wR_2 (all data) = 0.0470, 0.1060; refined against $|F^2|$; largest residual peak = 0.213 e Å^{-3}. CCDC-632450 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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