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Ionic Solid-State Dimers and Polymers Derived from Imidazolium Dicarboxylic Acids

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Abstract: A series of imidazolium dicarboxylic acids have been prepared from the reaction of the 1,3-bis(carboxymethyl)imidazolium zwitterion with the Brønsted acids HX (X = F, Br, Cl, ClO_4). The structures of these acids have been established in the solid state by single-crystal X-ray diffraction, which revealed that the cations and anions form strong hydrogen bonds through O−H···X interactions, leading to the formation of dimeric and polymeric networks. These acids react with elemental zinc and cobalt to form stable polymeric coordination complexes, some of which have also been characterised by X-ray diffraction.

Keywords: Brønsted acids · coordination polymers · hydrogen bonds · ionic liquids · solid-state structures

Introduction

Coordination polymers, constructed from the simplest of organic or inorganic precursors, form some of the most remarkable network structures with intriguing architectural features.[1,2] Not only are they aesthetically pleasing, many also represent models, providing insights into network interactions.[3] In recent years, there has been a growing interest in this area, especially in the field of porous coordination polymers, given their potential application in separation, storage and catalysis.[1–4] Coordination polymers involving metal centres are particularly interesting, as their rich coordination chemistry provides access to a wide variety of different network designs and topologies. The use of aromatic linker motifs further expands the scope of the field, allowing the development of functionalised structures with desirable properties.[1–5]

Concurrently, there has been a rapid growth in the research and development of imdazolium-based ionic liquids, often considered to have polymeric structures in the liquid state, which correspondingly lead to their high viscosities.[6] Much of the focus of ionic liquid research has been on their application as reaction media.[6,7] Imidazolium-based ionic liquids are particularly versatile and may be modified to give specific chemical and physical properties.[8,9] We have been interested in developing acidic imidazolium-based ionic liquids,[10,11] given their wide range of applications, for example in Friedel–Crafts reactions,[12] esterification,[13] and in many other important reactions.[14] Notably, we have developed imidazolium carboxylic zwitterions (Scheme 1) from which a range of different acidic ionic liquids can be prepared.[15]

Herein, we describe the synthesis and structural characterisation of a series of novel imidazolium-based dicarboxylic acids by the reaction of conventional Brønsted acids with imidazolium dicarboxylic zwitterions. These imidazolium dicarboxylic acids form linear polymers or dimers in the solid state that are based on hydrogen-bonding and π-stacking interactions, depending on the size of the anion. The subsequent use of the acids as bidentate heterocyclic aromatic linkers, leading to new coordination polymers containing zinc and cobalt, is also explored.

Results and Discussion

The zwitterionic imidazolium carboxylate **1** is a natural product that can be isolated from the Billard reaction.[16,17] However, **1** can also be readily synthesised from the reaction of *N*-(trimethylsilyl)imidazole with two equivalents of methyl chloroacetate, followed by ester hydrolysis and neutralisation of one carboxylic acid group with an organic

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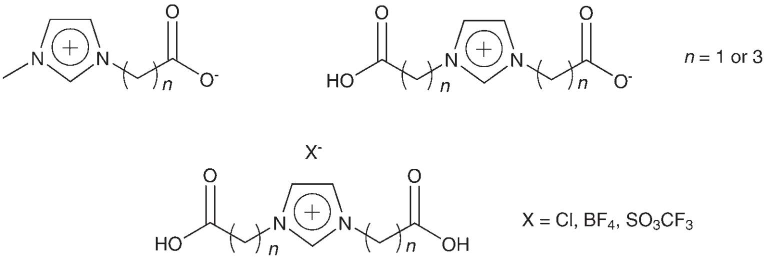
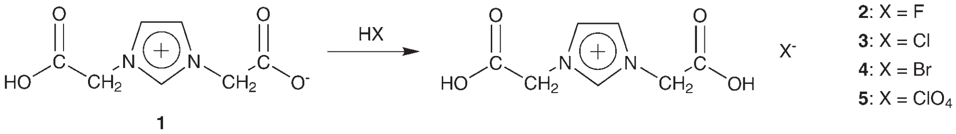


Scheme 1. Structures of imidazolium carboxylic zwitterions (top) and imidazolium dicarboxylic acids (bottom).

base. The details of this synthetic procedure were described previously.[15]

The target imidazolium dicarboxylic acids **2**–**5** were synthesised from the reaction of **1** with an excess of the corresponding aqueous Brønsted acid, namely HF, HCl, HBr and $HClO_4$ (Scheme 2). The products were isolated in high yield as white powders that are stable at room temperature. The compounds **2**–**4** are stable even at temperatures as high as 250 °C under vacuum. However, beyond their melting point temperatures of 250–280 °C, they decompose rapidly. All the salts are insoluble in common organic solvents such as dichloromethane, chloroform, acetone and methanol, but they are highly soluble in water.

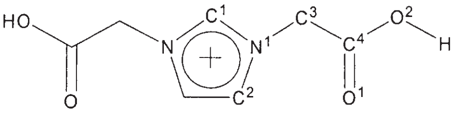


Scheme 2. Synthesis of imidazolium dicarboxylic acid halides/chlorate.

The compounds have been characterised by solid-state IR and solution NMR spectroscopy and electrospray ionisation mass spectrometry (ESI-MS). The ^{1}H and ^{13}C NMR spectra of the acids **2**–**5** in D_2O are nearly identical, with minor differences in chemical shifts, as the polymeric structure is not retained in solution. In particular, the peak at $\delta = 8.70$ ppm, which is assigned to the aromatic proton at C1 (refer to Table 1), was found to rapidly diminish in intensity at room temperature, suggesting fast H–D exchange with the deuterated solvent, demonstrating the acidity of the imidazolium C-H atom residing between the two electronegative N atoms, typical of this class of compound. The IR spectra of **2**–**5** show strong absorptions between 1720–1730 cm^{-1}, which are assigned to carboxylic C=O stretches. In **3**, **4** and **5**, medium-strong absorptions in the region 2450–2900 cm^{-1} are observed and are assigned to C−H···X stretches (X = Cl, Br and ClO_4). In contrast, only weak absorptions are observed for the C−H···F interaction in **2**. Similar observations have also been made in other imidazolium systems with alkyl-,[18] nitrile-[19] and alkynyl-functionalised[20] side chains. Incidentally, this absorption is not found in the halide-free zwitterion **1**. The ESI-MS of the acids also show typical anion–cation aggregation in aqueous solutions, which are strongly concentration-dependent and characteristic of imidazolium salts.[21]

Solid-state structure determinations of 2–5: Although several ionic imidazolium carboxylic acids and zwitterions are known, very few of their structures have been determined in the solid state.[15,22] For **2**–**5**, attempts to grow crystals suitable for X-ray diffraction using conventional techniques, for example, vapour and liquid diffusion, and slow solvent evaporation, were unsuccessful. This is partly because the compounds are only soluble in water, unlike other similar imidazolium acids with longer pendant side arms, which are also soluble in polar organic solvents such as acetonitrile.[15] Attempts to crystallise the compounds using mixed solvent combinations, such as water–THF, water–acetone, water–acetonitrile, or water–methanol resulted in the formation of amorphous powders. We therefore took the approach to crystallise the compounds directly from the reaction mixture. Thus, **1** was dissolved in the corresponding aqueous acid, heated gently to 40 °C and slowly cooled to 2 °C, to yield single crystals suitable for X-ray diffraction analysis.

Table 1. Selected bond lengths [Å] and angles [°], including H-bonding and intermolecular ring-ring stacking parameters[a] of **2**–**5**.



	2	**3**	**4**	**5**
N1−C1 [Å]	1.330(2)	1.341(3)	1.334(4)	1.328(2)
N1−C2 [Å]	1.385(3)	1.402(3)	1.379(4)	1.383(2)
N1−C3 [Å]	1.458(2)	1.463(3)	1.463(4)	1.461(2)
C3−C4 [Å]	1.515(3)	1.526(4)	1.510(5)	1.508(3)
C4−O1 [Å]	1.206(3)	1.193(3)	1.215(4)	1.206(2)
C4−O2 [Å]	1.319(2)	1.339(3)	1.316(4)	1.333(2)
C1-N1-C2 [°]	108.61(17)	108.6(2)	109.0(3)	108.89(14)
C3-C4-O2 [°]	111.20(17)	109.1(2)	109.8(3)	111.23(14)
O2···H···X [Å]	2.4297(15)	3.006(2)	3.107(2)	2.838(2)[b]
Γ [Å]	4.728(2)	4.662(2)	5.015(2)	4.860(2)
Z [Å]	3.711	3.654	3.349	3.571
X [Å]	2.929	2.895	3.733	3.296
θ [°]	38.28	38.39	48.11	42.71

[a] These are the centroid to centroid distance (Γ), the vertical displacement (Z), the horizontal displacement (X) and the angle between the normal vertex to the centroid of the adjacent ring (θ). Measurement and calculation of the ring–ring stacking parameters were made using PLATON in the WinGX software package.[24] [b] X refers to the closest O atom.

The bond lengths and angles of the imidazolium rings in **2**–**5** are only marginally different from other imidazolium systems that have been determined by X-ray diffraction.[15,23] The N1−C1 distances range from 1.328(2)–1.341(3) Å and the N1−C2 distances from 1.379(4)-1.402(3) Å, which are typical values, and therefore they do not appear to be affected by the nature of the anion. Hydrogen-bonding interactions are observed in all of the complexes, especially between the acidic carboxylic protons and the anions. In **2** and **3**, the anions bridge two adjacent protons through hydrogen-bonding, while in **4** and **5**, the anions are H-bonded singly to a carboxylic acid proton. There are also interactions between the anions with protons on adjacent imidazolium rings, but these interactions are weaker (longer). It is not possible to accurately determine the position of the carboxylic protons in the structures from the available X-ray diffraction data; however, the strength of H-bonding interactions could be inferred from the distance between the carboxylic O-atom to the halide anion. As expected, the distances increase from $F^- < ClO_4^- < Cl^- < Br^-$ (see Table 1), indicating a decrease in the strength of the H-bond, which directly correlates with the decrease in electronegativity of the anion.

The size of the anion also exerts a significant influence on the macrostructure of the crystalline acids. In **2** and **3**, linear polymeric chains of imidazolium cations are formed (Figure 1), in which the small electronegative F^- and Cl^- ions bridge the cations. In contrast, **4** and **5** do not adopt extended structures since the imidazolium moieties dimerise through H-bonding between one of their carboxyl groups, with the Br^- or ClO_4^- ions H-bonded to the other carboxyl group (Figure 2). The fact that the presence of the electronegative oxygen centres in ClO_4^- does not favour the formation of polymeric chains suggests that the size of the anions is the main factor in the determining the macrostructure. In addition, significant π-stacking interactions are observed in **2** and **3**, with a centroid to centroid distance of 4.728(2) and 4.662(2) Å, respectively, between adjacent *syn*-facial rings (Table 1), giving rise to uniform layers of linear polymers. Longer π-stacking interactions are found in **4** and **5**, with distances of 5.015(2) and 4.860(2) Å between nearest rings, which are stacked *anti*-facially. The horizontal displacement distances were also larger, implying a poorer overlap in the π-stacking arrangements.

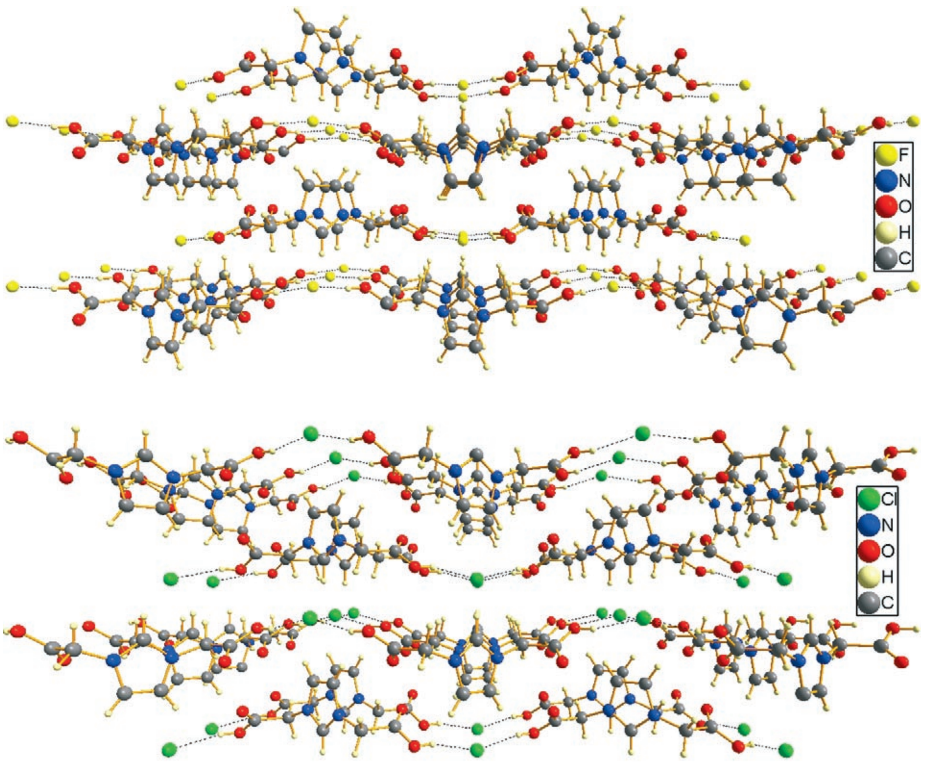


Figure 1. Packing diagram of **2** (top) and **3** (bottom), viewed along the *b* axes. Atoms are presented as spheres with arbitrary radii.

Formation of coordination polymers from acids 3 and 4: Multidentate carboxylic acids are excellent ligands for the synthesis of coordination polymers and have been used extensively to develop polymers with unusual topologies and conformations.[24] Usually, coordination polymers derived from carboxylic acids are synthesised by deprotonating the acids with basic metal salts, thereby generating the carboxylic anions that subsequently coordinate to the metal centre.[25] Conventional zinc carboxylate complexes have been prepared by the reaction of the desired carboxylic acids with zinc salts such as $ZnSO_4$, $Zn(ClO_4)_2$, $Zn[N(SiMe_3)_2]_2$ and $Zn(NO_3)_2$.[26] However, we have found that **3** and **4** are sufficiently strong acids to react directly with elemental zinc.[27,28] Zinc-containing imidazolium carboxylates $\{[ZnCl(H_2O)(C_7H_7N_2O_4)](H_2O)\}_\infty$ (**6**) and $\{[ZnBr(H_2O)(C_7H_7N_2O_4)](H_2O)\}_\infty$ (**7**) were thus obtained by the direct reaction of zinc with an aqueous solution of **3** and **4**, respectively, at room temperature. The structure of **7** was reported previously in a preliminary communication.[27] The reaction is slow and takes several days to complete with the products being obtained in near quantitative yield.

Upon dissolution in water, the macromolecular structures of **6** and **7** are cleaved, and therefore, the spectroscopic data recorded in aqueous solution is uninformative. The solid-state IR spectra of **6** and **7** are comparable to **2**–**5**. The main differences are the presence of

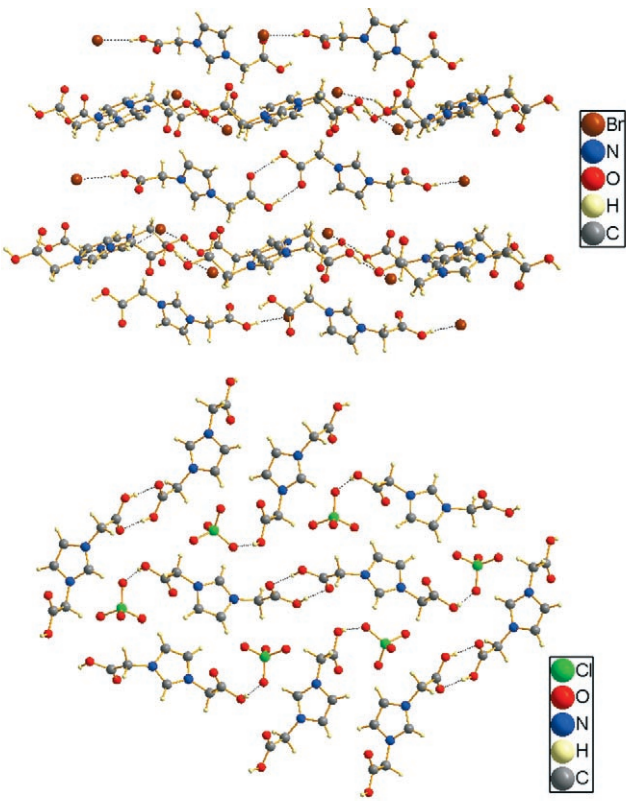


Figure 2. Packing diagram of **4** (top) and **5** (bottom), viewed along the *a* axes. Atoms are presented as spheres with arbitrary radii.

strong (broad) O−H absorptions at 3500 cm^{-1}, due to the presence of bulk water molecules, and the lowering of $C=O$ absorptions to 1565–1687 cm^{-1}. The shift of $C=O$ stretching frequencies towards lower frequencies, by about 150 cm^{-1}, suggests a weakening of carboxyl bond, due to the co-ordination to the zinc centre.

As shown in Figure 3, the co-ordination sphere around the zinc centre in **6** is tetrahedral, comprising two carboxylate bonds, a coordinated water molecule and a chloride ligand. The Zn−O bond lengths in **6** are comparable to those in **7** and other known Zn–carboxylate networks.[27,29] The macrostructure of **6** and **7** can be described as a helical channel array, assembled from $ZnX(H_2O)$-imidazolium dicarboxylate moieties ($X = Cl$ and Br), with intra-helical H-bonds and π-stacking interactions between the imidazolium molecules (Figure 4). The helix is formed with imidazolium rings stacked together at a centroid to centroid distance of 6.155(2) Å and with their bridging pendant arms directed towards the same direction perpendicular to the aromatic plane, as opposed to **2**–**5**, where the bridging arms are extended in opposite directions. The interesting feature of the structure is the presence of uncoordinated water molecules within the helical channels, their characterisation in **7** by solid-state NMR spectroscopy was described in the previous report,[27] summarised and compared with water-channel protein. As in **7**, the water molecules in **6** are held in place by extensive H-bonding with the zinc imidazolium carboxylate helical backbone and are instrumental in defining the macrostructure, since the removal of water by heating inadvertently results in the loss of structural order. The inner dimensions of the zinc imidazolium channel in **6** are marginally smaller than those in **7**,[27] which is not unexpected since the coordinated halide ligands are located on the exterior of the helix and therefore do not contribute significantly to the dimensions of the pore.

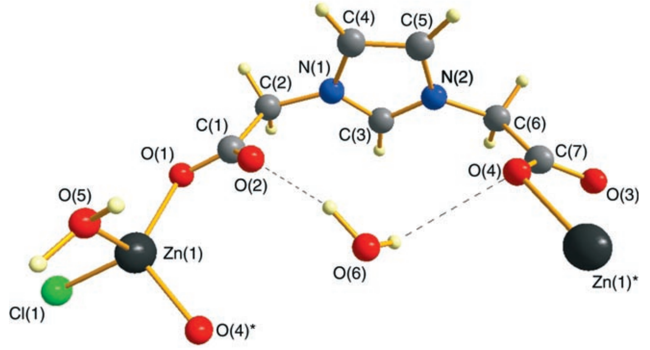


Figure 3. Structure of **6**; atoms are presented as spheres with arbitrary radii.

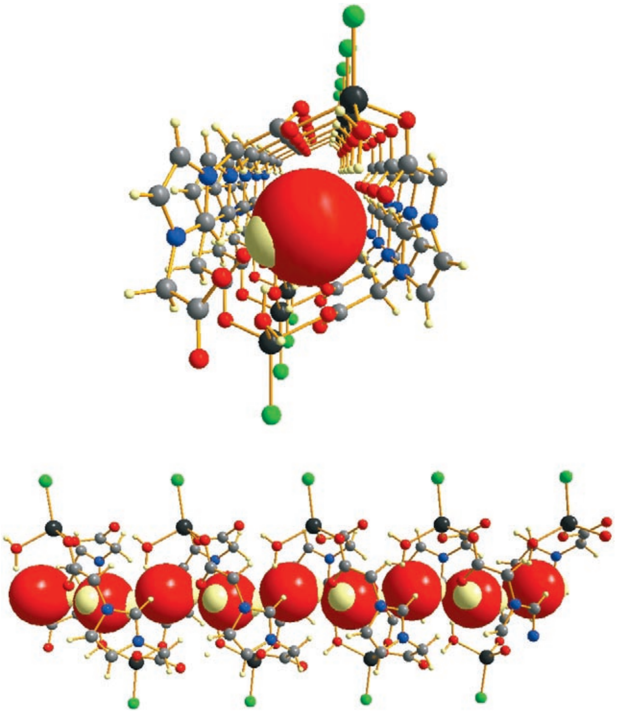


Figure 4. View of zinc imidazolium dicarboxylate helix in **6** along the *b* axis (top) and *c* axis (bottom). Free water molecules represented by spheres at van der Waals radii. The remaining atoms are presented as spheres with arbitrary radii. (refer to Figure 3 for detailed colour scheme).

Reaction of **4** with elemental cobalt yielded the pink cobalt imidazolium coordination polymer {[$Co(H_2O)_4$-

$(C_7H_7N_2O_4)]Br(H_2O)\}_\infty$ (**8**). As with **6** and **7**, the cobalt complex **8** was found to be only soluble in water and not in organic solvents such as acetone, dichloromethane, methanol or DMSO, although the polymeric structure is not retained in aqueous solution. In the solid state, the coordination sphere around the cobalt centre in **8** is octahedral, with two *cis*-carboxylate bonds and four coordinated water molecules (Figure 5). The bidentate imidazolium ligands bridge the cobalt centres, forming extended cobalt imidazolium carboxylate chains. Unlike **6** and **7**, the bromide is not coordinated directly to the cobalt centre and therefore, the cobalt imidazolium carboxylate chains are positively charged. Nonetheless, the Co−O distances, 2.073(8)-2.151(7) Å, are similar to those in other cobalt dicarboxylate systems.[30]

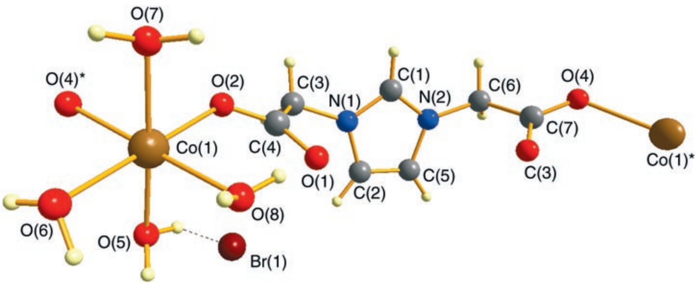


Figure 5. Structure of **8**; atoms are presented as spheres with arbitrary radii. The uncoordinated water molecule is disordered and omitted for clarity.

The macrostructure of **8** may be described as ribbons, composed of two interlocking cobalt imidazolium carboxylate polymeric chains (i.e. chain-pairs), separated by a discrete layer of bromide anions (Figure 6). This layer also contains an uncoordinated water molecule, per cobalt imidazolium carboxylate unit, which is poorly defined and disordered. As with **6** and **7**, extensive H-bonding interactions are found throughout the macrostructure and appear to be crucial in maintaining its overall integrity. Importantly, the polymeric chain pairs are held together by extensive intermolecular H-bonds between a coordinated water molecule and two carboxylate O atoms on the opposite chain. These interactions allow the two chains to "zip" together throughout the structural framework. The pendant bridging arms are also oriented in the same direction, similar to **6** and **7**. The uncoordinated water molecules, which are poorly defined and disordered, are H-bonded to the alkyl C-H protons on the cobalt imidazolium backbone. The uncoordinated bromide anions occupy discrete bands in the macrostructure, held in place by H-bonds between the ribbons of cobalt imidazolium carboxylate chains. The chain-pairs are themselves stacked closely together with a centroid to centroid distance of 5.194(1) Å between the layers of imidazolium rings.

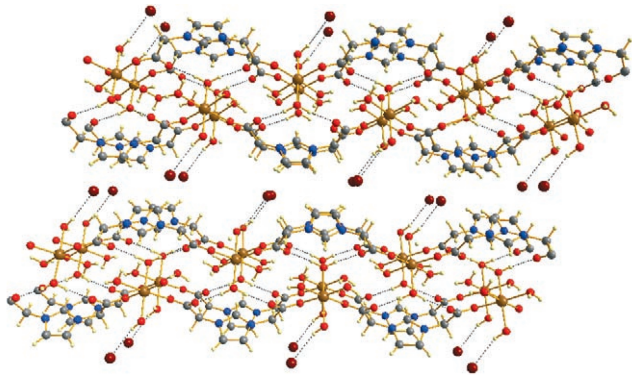


Figure 6. View of cobalt imidazolium dicarboxylate **8** along the *a* axis. Atoms are presented as spheres with arbitrary radii (refer to Figure 5 for detailed colour scheme). The uncoordinated water molecules are omitted for clarity.

Conclusion

A series of ionic imidazolium dicarboxylic acids halide/chlorate salts has been synthesised and characterised by spectroscopic methods and X-ray crystallography. In the solid state, their crystalline structures are found to be largely dependent on the size of the anion, with small anions, that is, F^- and Cl^-, favouring long linear polymeric chains, whereas large anions, that is, Br^- and ClO_4^-, favour dimeric units. The acids are strong enough to react directly with elemental metals, and in the case of zinc and cobalt, coordination polymers are formed. The structural characteristics of the bidentate imidazolium dicarboxylate ligand are crucial in the formation of these coordination polymers. Firstly, different bonding directions can be achieved through its flexible coordinating pendant arms, giving rise to different structural conformations. Secondly, the presence of the heterocyclic aromatic ring system favours ordering in the macrostructure through π-stacking interactions. With the vast library of potential metal candidates, the imidazolium dicarboxylic acid ligand could be exploited for the development of other metallic coordination polymers, potentially with tuneable topologies and properties.

Experimental Section

General: Compound **1** was prepared according to a literature method.[15] All other materials were purchased from Aldrich and were used without further purification. IR spectra were recorded on a Perkin-Elmer FT-IR 2000. NMR spectra were measured in D_2O on a Bruker DMX 400, using $SiMe_4$ for ^1H and ^{13}C as external standards at 20 °C, and the chemical shifts are given in ppm with reference to the standards. Electrospray ionisation mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on samples diluted in water using a literature protocol.[31] Elemental analyses were carried out at the EPFL.

Synthesis of 2: Compound **1** (1.84 g, 0.010 mol) was dissolved in water (4.0 mL) in a Teflon-tube and heated at 40 °C until completely dissolved. Aqueous HF (4.0 mL, 48 % H_2O solution) was added. The resulting solution was stirred for 10 min and the solvent was removed under reduced pressure. The remaining solid was washed with acetone and diethyl ether, and then filtered to yield a white powder. Yield: 92%, M.p. 250°C (decomp); ESI-MS: 184 $[C_7H_9N_2O_4]^+$; ^1H NMR (400.1 MHz, D_2O): $\delta =$ 8.69 (s, 1H), 7.36 (s, 2H), 4.88 ppm (s, 4H); ^{13}C NMR (100.6 MHz, D_2O): $\delta = 172.4$, 137.2, 123.1, 51.9 ppm; IR: $\tilde{\nu} = 3322$, 3125, 3001, 2960, 1724, 1662, 1572, 1163 cm^{-1}; elemental analysis calcd (%) for $C_7H_9FN_2O_4$ (204.16): C 41.18, H 4.44, N 13.72; found: C 41.41, H 4.49, N 13.79.

Synthesis of 3, 4 and 5: Compound **1** (1.84 g, 0.010 mol) was dissolved in water (4.0 mL) and heated at 40°C until completely dissolved. Aqueous HX (4.0 mL, X = Cl 37%, Br 48%, ClO_4 20%) was added. The resulting solution was stirred for 10 min and the solvent was removed under reduced pressure. The remaining solid was washed with acetone and diethyl ether to give the product as white powders. Spectroscopic characterisation of **3** has been previously reported.[15]

4: Yield 95%, M.p. 280°C (decomp); ESI-MS: 184 $[C_7H_9N_2O_4]^+$; ^1H NMR (400.1 MHz, D_2O): $\delta = 8.70$ (s, 1H), 7.38 (s, 2H), 4.90 ppm (s, 4H); ^{13}C NMR (100.6 MHz, D_2O): $\delta = 172.3$, 137.1, 123.0, 52.0 ppm; IR: $\tilde{\nu} = 3106$, 3062, 2981, 2817, 2516, 1722, 1562, 1407, 1236, 1198, 1171, 976, 864, 762 cm^{-1}; elemental analysis calcd (%) for $C_7H_9BrN_2O_4$ (265.07): C 31.72, H 3.42, N 10.57; found: C 31.61, H 3.49, N 10.69.

5: Yield: 97%. M.p. 110°C; ESI-MS: 184 $[C_7H_9N_2O_4]^+$; ^1H NMR (400.1 MHz, D_2O): $\delta = 8.69$ (s, 1H), 7.36 (s, 2H), 4.80 ppm (s, 4H); ^{13}C NMR (100.6 MHz, D_2O): $\delta = 172.0$, 137.4, 123.0, 52.1 ppm; IR: $\tilde{\nu} =$ 3159, 3025, 2900–2850 (broad peaks), 1726, 1617, 1568, 1407, 1259, 1179, 1049, 970, 889, 745, 669, 618 cm^{-1}; elemental analysis calcd (%) for $C_7H_9ClN_2O_8$ (284.61): C 29.54, H 3.19, N 9.84; found: C 29.41, H 3.20, N 9.69. *(While no incident occurred during the synthesis of the compound, caution has to be taken given the propensity of chlorate compounds to explode upon prolonged heating at elevated temperatures!).*

Synthesis of 6: A mixture of elemental zinc (1.50 g, 0.023 mol) and **2** (2.21 g, 0.010 mol) in water (20 mL) was stirred for 10 days at room temperature. The mixture was filtered and the filtrate concentrated to 10 mL. Upon standing at room temperature for seven days, colourless crystals of **6** were obtained. Yield: 96%. ^1H NMR (400.1 MHz, D_2O): $\delta =$ 8.80 (s, 1H), 7.40 (s, 2H), 5.06 ppm (s, 4H); ^{13}C NMR (100.6 MHz, D_2O): $\delta = 172.6$, 138.1, 126.2, 52.0 ppm; IR: $\tilde{\nu} = 3450$, 3151, 3108, 1587, 1563, 1438, 1398, 1289, 1175, 770, 685 cm^{-1}; elemental analysis calcd (%) for $C_7H_{11}ClN_2O_6Zn$ (320.01): C 26.27, H 3.46, N 8.75; found: C 26.41, H 3.53, N 8.70.

Synthesis of 8: A mixture of elemental cobalt (1.20 g, 0.020 mmol) and **3** (2.65 g, 0.010 mol) in water (20 mL) was stirred for 10 days at room temperature. The mixture was filtered and the pink filtrate concentrated to 10 mL. Upon standing at room temperature for seven days, pink crystals of **8** were obtained. Yield: 86%. ^1H NMR (400.1 MHz, D_2O): $\delta = 8.68$ (s, 1H), 7.36 (s, 2H), 4.99 ppm (s, 4H); ^{13}C NMR (100.6 MHz, D_2O): $\delta =$ 172.4, 138.2, 126.1, 51.8 ppm; IR: $\tilde{\nu} = 3450$, 3094, 1567, 1444, 1383, 1348, 1176, 846, 773, 666 cm^{-1}; elemental analysis calcd (%) for $C_7H_{17}CoBrN_2O_9$ (412.06): C 20.40, H 4.16, N 6.80; found: C 20.41, H 4.23, N 6.79.

Crystallisation of 2–5 for X-ray diffraction analysis: Compound **1** was dissolved in minimum amount of the aqueous HF (48%) solution at 40°C. The resulting solution was slowly cooled to 2°C overnight to yield crystals of **2** suitable for X-ray structure analysis. Crystals of **3**, **4** and **5** were obtained in a similar manner using the aqueous solution of HCl (37%), HBr (48%) and $HClO_4$ (20%), respectively.

Crystallographic structure determination: Data collection for **2–5**, **6** and **8** was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD or MAR345 IPDS at 140 K. Data reduction was performed by using CrysAlis RED.[32] Structure solution and refinement was performed by using SHELXTL software package for all compounds,[33] except for the structure solution of compounds **2** and **8**, which was performed by using SiR97.[34] Structures were refined by full-matrix least-squares refinement (against F^2) with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined isotropically. Empirical absorption corrections were applied to **4**, **7** and **8** using DELABS.[35] Graphical representations of the structures were made with Diamond.[36] Relevant crystallographic data are compiled in Table 2. CCDC-280031 and CCDC-280036 contain 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.

Table 2. Crystallographic data for **2**, **3**, **4**, **5**, **6** and **8**.

	2	**3**	**4**	**5**	**6**	**8**
formula	$C_7H_9FN_2O_4$	$C_7H_9ClN_2O_4$	$C_7H_9BrN_2O_4$	$C_7H_9ClN_2O_8$	$C_7H_{11}ClN_2O_6Zn$	$C_7H_{17}BrCoN_2O_9$
fw	204.16	220.61	265.07	284.61	320.00	412.07
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_12_12$	$P2_12_12$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	12.668(4)	13.602(3)	10.193(2)	5.3715(13)	9.776(3)	5.1945(9)
b [Å]	4.7275(6)	4.6617(10)	9.1761(15)	13.086(2)	6.1552(18)	11.6926(14)
c [Å]	6.973(2)	7.5645(14)	10.797(2)	15.4295(12)	19.019(3)	12.5698(18)
α [°]	90	90	90	90	90	107.633(13)
β [°]	90	90	108.54(2)	91.428(13)	98.150(18)	97.626(13)
γ [°]	90	90	90	90	90	90.406(13)
volume [$Å^3$]	417.59(19)	479.64(17)	957.5(3)	1084.3(3)	1132.9(5)	720.24(18)
Z	2	2	4	4	4	2
ρ_{calcd} [$g\,cm^{-3}$]	1.624	1.528	1.839	1.744	1.876	1.900
$F(000)$	212	228	528	584	648	414
μ [mm^{-1}]	0.147	0.389	4.284	0.392	2.422	4.008
temperature [K]	140(2)	140(2)	140(2)	140(2)	140(2)	140(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
measured reflections	2640	2916	5554	6540	6188	4179
unique reflections	707	812	1684	1887	1984	2223
unique reflections [$I > 2\sigma(I)$]	686	705	1385	1641	1842	1999
no. of data/restraints/parameters	707/0/84	812/0/83	1684/0/152	1887/0/200	1984/6/166	2223/18/210
R[a][$I>2\sigma(I)$]	0.0360	0.0312	0.0309	0.0365	0.0400	0.0867
$wR2$[a] (all data)	0.0909	0.0596	0.0776	0.0993	0.1093	0.2251
GooF[b]	1.121	0.949	0.999	1.116	1.090	1.170

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)2]/\Sigma\ [w(F_o^2)^2]\}^{1/2}$. [b] $\mathrm{GooF} = \{\Sigma[w(F_o^2 - F_c^2)2]/(n-p\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

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