

Metal–Organic Frameworks Derived from Imidazolium Dicarboxylates and Group I and II Salts

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A series of coordination polymers containing Group I or II metal ions, connected via an imidazolium-centered dicarboxylate ligand, have been isolated from water and characterized by single crystal X-ray diffraction. All the structures incorporate water molecules that adopt a range of different structural motifs.

Introduction

The systematic design of coordination polymers, sometimes referred to as metal–organic frameworks (MOFs), is a fascinating and challenging area of research.¹ The synthesis of novel supramolecular architectures such as molecular boxes, knots, and helicates, as well as coordination polymers, has advanced rapidly in the past few years.^{2,3} Self-assembly has proven to be a versatile approach for the preparation of nanoscale porous materials. The key to such an organization process involves hydrogen-bonding,⁴ ion-pairing,⁵ and dative interactions.⁶ Porous frameworks containing metals are particularly interesting⁷ because they may be applied in, for example, hydrogen storage, ion-exchange resins, and catalysis.⁸ Also, such materials could have intriguing electrical and magnetic properties.⁹

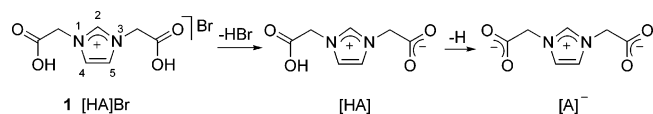
Multidentate carboxylic acids are excellent ligands for the synthesis of coordination polymers affording structures with a diverse range of topologies and conformations,¹⁰ with the carboxylate group able to coordinate to a metal center as a mono-, bi-, or multidentate ligand. Meanwhile, recent reports with ionic liquids used as both solvent and template in synthesis of zeolite analogues¹¹ indicate the potential of such materials in the synthesis of coordination polymers. A number of aluminum coordination polymers have been prepared from imidazolium bromides or ammonium chlorides in which the cationic and anionic components of the precursors are included in the final structures.^{11c} Carboxylic acids based on imidazolium cations bearing carboxylic groups and halide anions can be considered to be ionic liquids; these compounds have been known for many years.¹² However, to the best of our knowledge, we are the first to investigate cationic carboxylic acids, in an effort to explore

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- (1) (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: New York, 1995. (b) Haiduc, I.; Edelman, F. T. *Supramolecular Organometallic Chemistry*, Wiley-VCH: New York, 1999.
- (2) (a) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511. (d) May, L. J.; Shimizu, K. H. *Z. Kristallogr.* **2005**, *220*, 364. (e) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3.
- (3) (a) Galet, A.; Munoz, M. C.; Real, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 14224. (b) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542. (c) Bu, X.-H.; Tong, M.-L.; Chang, H.-C.; Kitagawa, S.; Batten, S. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 192. (d) Wang, X.-L.; Qin, C.; Wang, E.-B.; Xu, L.; Su, Z.-M.; Hu, C.-W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5036. (e) Sreenivasulu, B.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5769.
- (4) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; Brinke, G. T.; Ikkala, O. *Science* **1998**, *280*, 557.
- (5) Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1998**, *5*, 41.
- (6) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000.
- (7) Stuart, R. B. *CrystEngComm*, **2001**, *18*, 1.
- (8) (a) Müller, A.; Das, S. K.; Talismanov, S.; Roy, S.; Beckmann, E.; Bögge, H.; Schmidtman, M.; Merca, A.; Berkle, A.; Allouche, L.; Zhou, Y.; Zhang, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5039. (b) Rao, C. N. R.; Natarajan, S.; Vaidyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (c) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- (9) (a) Wang, S.; Zuo, J.-L.; Zhou, H.-C.; Choi, H. J.; Ke, Y.; Long, J. R.; You, X.-Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 5940. (b) Wang, X.-Y.; Wang, L.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674.
- (10) (a) Erxleben, A. *Coord. Chem. Rev.* **2003**, *246*, 203. (b) Jiang, P.; Guo, Z. *Coord. Chem. Rev.* **2004**, *248*, 205. (c) Ye, B.-H.; Tong, M.-L.; Chen, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 545.
- (11) (a) Adams, C. J.; Bradley, A. E.; Seddon, K. R. *Aust. J. Chem.* **2001**, *54*, 679. (b) Jin, K.; Huang, X.; Pang, L.; Li, J.; Appel, A.; Wherland, S. *Chem. Commun.* **2002**, 2872. (c) Cooper, E. R.; Andrews, C. D.; Wheathley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. *Nature* **2004**, *430*, 1012. (d) Liao, J.-H.; Wu, P.-C.; Bai, Y.-H. *Inorg. Chem. Commun.* **2005**, *8*, 390. (e) Parnham, E. R.; Morris, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 2204. (f) Parnham, E. R.; Wheathley, P. S.; Morris, R. E. *Chem. Commun.* **2006**, 380.

the coordination ability of the anion (halide) and the functionalities of the carboxylic groups.¹³ The coordination chemistry of imidazolium-based carboxylic acids differs significantly from conventional neutral carboxylic acids, involving not only the coordination of the carboxylate groups but also, in many instances, coordination of the counteranion to the transition metal center^{13b} or inclusion of the counteranion as a guest.^{13c} In addition, the majority of these investigations dealing with coordination polymers using carboxylic groups as connectors employ transition metal centers as connectors,¹⁰ and less effort has been devoted to polymeric frameworks containing Group I and II metals.¹⁴ The involvement of halides as ligands or to balance charge is common in synthetic coordination polymers with transition metal connectors (e.g., Zn, Cu, and Ag),¹⁰ but the inclusion of halides in Group I or II metal-based coordination polymers is elusive. The most recent examples of barium–carboxylate polymers, for example, catena-poly[triaquabarium(II)]-di-*m*-6-amino-3-methyl-5-nitrosopyrimidine-2,4(1H,3H)-dionato,^{14f} or *m*-phenylenedioxyacetate¹⁵ frameworks were synthesized from barium chlorides, but the final structures do not contain chloride.

In our previous reports, we found that 1,3-biscarboxy-alkylimidazolium salts such as **1** are relatively strong acids, capable of oxidizing elemental zinc to give a helical coordination polymer incorporating a one-dimensional water chain^{13b} or two-dimensional water sheet.^{13c} In **1** and the deprotonated forms of **1**, the zwitterion [HA] and the anionic zwitterion [A][−], the hydrogen atoms in the imidazolium backbone (including the aromatic H atoms at the 2, 4, and 5 positions and the hydrogen atoms in the sidearms) are, to some extent, acidic and can act as hydrogen-bond donors helping the host–guest molecules such as water or halides.¹³



Thus, we became interested in utilizing **1** as a scaffold for the preparation of metal–carboxylate polymers, harnessing the strong acidic character of all the hydrogen atoms in the imidazolium backbone to incorporate the halide anion

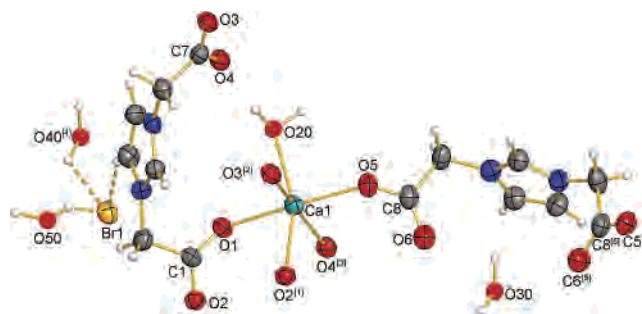


Figure 1. ORTEP plot of **2** (water molecules are represented as ball-and-stick figures); ellipsoids are drawn at the 40% probability level. Symmetry operations: $1\ 1-x, 1-y, -z$; $2\ 1-x, 1-y, 1-z$; $3\ 1.5-x, 1-y, -0.5+z$; $4\ 0.5+x, 1.5-y, 0.5-z$; $5\ x, 0.5-y, z$. Selected bond lengths (Å): Ca(1)–O(1) = 2.341(5), Ca(1)–O(2)¹ = 2.348(4), Ca(1)–O(3)² = 2.339(5), Ca(1)–O(4)³ = 2.404(5), Ca(1)–O(5) = 2.267(5), Ca(1)–O(20) = 2.390(5).

and potentially water molecules into Group I and II coordination polymers.

Results and Discussion

Treatment of an aqueous solution of the carboxylate bromide **1** with 1 equiv of CaCO₃ gave complex **2** (isolated in a low yield after repeated recrystallization). The composition of the product corresponds to Ca₂[A₃Br]. In contrast, treatment of **1** with SrCO₃ or BaO affords **3** and **4** in quantitative yield with compositions of Sr[ABr] and Ba[AABr], respectively.¹⁶

In principle, the calcium, strontium, or barium cations can react with **1** to form independent molecules MA₂ and MBr₂. Alkylimidazolium halides are often converted into room-temperature ionic liquids using this process via reaction of the halide salts with Group I metal salts, such as potassium tetrafluoroborate. However, the bromide forms short hydrogen bonds with the H atoms of the imidazolium cation in **2** and **3** suppressing the formation of CaBr₂ or SrBr₂. Also, the bromide forms hydrogen bonds with water molecules which presumably also help to trap them in the coordination polymer, and in **4**, the bromide even coordinates to the barium ion.

Bonding within the imidazolium moiety in **2–4** is of a routine nature with bond distances and angles identical within experimental errors and in good agreement to other known imidazolium salt structures.¹³ The C–O bond lengths in the carboxylate group range between 1.240(7) and 1.262(4) Å, indicating an even delocalization of the negative charge, in contrast to 1.202(2) and 1.330(4) Å in the related acid 1,3-biscarboxypropylimidazolium chloride precursor.^{13a} Bond lengths and angles of the carboxylic groups are also within the range found in other carboxylic coordination polymers.^{17–19}

(16) Spectroscopic data of the coordination polymers **2–4** following dissolution in water indicate that the polymeric network does not prevail and complete solvation of the ionic components takes place. The ¹H and ¹³C NMR spectra of **2–4** in D₂O at room temperature are very similar to that of **1**. The IR spectra of **2–4** in the solid state display middle-strong absorptions at 3662–3669 and 3300–3450 cm^{−1} for the H–O–H vibration of the water molecules. The C=O vibration of the carboxylic groups are shifted to 1589–1606 cm^{−1}, as compared to the free carboxylic acids (at ca. 1700 cm^{−1}). See also ref 13a.

- (12) (a) Blackburn, G. M.; Dodds, H. L. H. *J. Chem. Soc., Perkin Trans. 2* **1974**, 377. (b) Alcalde, E.; Gisbert, M.; Perez-Garcia, L. *Chem. Lett.* **1992**, 12, 2357. (c) Barboiu, V.; Strebă, E.; Holerca, M. N.; Luca, C. *J. Macromol. Sci. Pure Appl. Chem.* **1995**, A32, 1385. (d) Alcalde, E.; Gisbert, M.; Perez-Garcia, L. *Heterocycles* **1996**, 4, 567.
- (13) (a) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem.–Eur. J.* **2004**, 10, 4886. (b) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J.; Antonijević, S.; Bodenhausen, G. *Angew. Chem., Int. Ed.* **2005**, 44, 5720. (c) Fei, Z.; Geldbach, T. J.; Zhao, D.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2005**, 44, 5200.
- (14) For recent reports on carboxylates containing main group elements, see: (a) Kedarnath, K.; Choudhury, A.; Natarajan, S. *J. Solid State Chem.* **2000**, 150, 324. (b) Hung, L.-C.; Kao, H.-M.; Lü, K.-H. *Chem. Mater.* **2000**, 12, 2411. (c) Uhl, W. *Chem. Soc. Rev.* **2000**, 29, 259. (d) Choi, C. T. S.; Anokhina, E. V.; Day, C. S.; Zhao, Y.; Taulelle, F.; Huguenard, C.; Gan, Z.; Lachgar, A. *Chem. Mater.* **2002**, 14, 4096. (e) Huang, Y.-F.; Lü, K.-H. *J. Chem. Soc., Dalton Trans.* **1998**, 4085. (f) Garzón, R. L.; Salido, M. L. G.; Low, J. N.; Glidewell, C. *Acta Crystallogr.* **2003**, C59, m255.
- (15) Gao, S.; Liu, J.-W.; Huo, L.-H.; Zhao, H. *Acta Crystallogr.* **2005**, C61, m348.

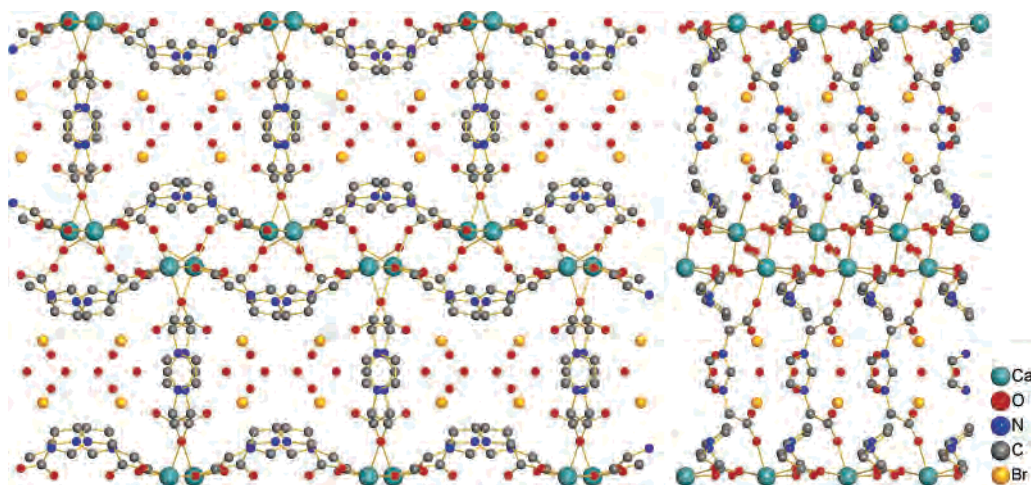


Figure 2. Crystal packing in **2** along the a axis (left) and the c axis (right); hydrogen atoms have been omitted for clarity.

The zwitterionic imidazolium anions in the four structures differ mainly with respect to the orientation of the carboxylate-functionalized alkyl chains relative to the plane of the imidazolium ring. In **2**, the substituents adopt a *cis* orientation; in **3**, they are *trans* to each other, while in **4**, both configurations are present in the crystal.

Compound **2** (empirical formula $\text{Ca}_2[\text{A}_3\text{Br}] \cdot 5\text{H}_2\text{O}$) contains four different water molecules per asymmetric unit, of which one is bonded to the calcium ion, two interact via hydrogen bonds with the bromide anion, and one “free” water molecule does not exhibit significant interactions with any of the other moieties. Each calcium is bound to one water molecule [$\text{Ca}(1)–\text{O}(20) = 2.390(5) \text{ \AA}$] and five different imidazolium cations via one of their carboxylate oxygen atoms, [$\text{Ca}(1)–\text{O} = 2.267–2.404 \text{ \AA}$], see Figure 1. The three-dimensional polymer consists of sinusoidal-shaped double layers of calcium ions, composed of rows of calcium cations [$\text{Ca}(1)–\text{Ca}(1) = 4.9820(5) \text{ \AA}$] that are linked via bridging imidazolium ligands. These layers are connected by bridging imidazolium carboxylate anions, as shown in Figure 2. Four of the carboxylate oxygen atoms bind to other calcium cations in the double layer and one bridges to the next layer. The bromide anion, which lies on a center of symmetry, is positioned between the layers, held in place by multiple, rather long, hydrogen bonds stemming from water molecules and imidazolium protons.

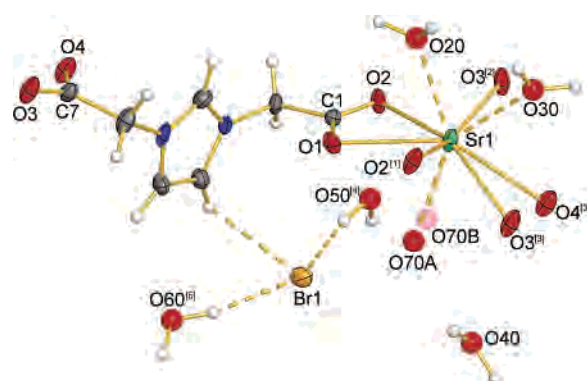


Figure 3. ORTEP plot of **3** (water molecules represented as ball-and-stick figures); ellipsoids are drawn at the 50% probability level. Symmetry operations: $1\ x, 0.5 - y, -0.5 + z$; $2\ 1 + x, 0.5 - y, 0.5 + z$; $3\ 1 + x, y, z$; $4\ x, 1.5 - y, 0.5 + z$; $5\ -x, 1 - y, 1 - z$. Selected bond lengths (\AA): $\text{Sr}(1)–\text{O}(1) = 2.735(4)$, $\text{Sr}(1)–\text{O}(2) = 2.709(4)$, $\text{Sr}(1)–\text{O}(2)^\prime = 2.553(4)$, $\text{Sr}(1)–\text{O}(3)^\prime = 2.548(4)$, $\text{Sr}(1)–\text{O}(3)^\prime = 2.688(4)$, $\text{Sr}(1)–\text{O}(4)^\prime = 2.751(4)$, $\text{Sr}(1)–\text{O}(20) = 2.576(4)$, $\text{Sr}(1)–\text{O}(30) = 2.640(5)$, $\text{Sr}(1)–\text{O}(70\text{A}) = 2.661(8)$.

The most striking difference between the structures of **2** and **3** is that in the latter case the metal–organic framework forms only a two-dimensional network (in contrast to the three-dimensional topology in **2**) of empirical formula $\text{Sr}[\text{ABr}] \cdot 5.5\text{H}_2\text{O}$, in which the polymeric sheets are held together via H bonds involving bromide anions and water molecules. There are 5.5 water molecules per asymmetric unit of which three are bound to the metal [$\text{Sr}(1)–\text{O} = 2.576(4)–2.661(8) \text{ \AA}$, one molecule being disordered], the remaining 2.5 free water molecules interact via H bonding with Br, the carboxylate moiety of the ligand, and other water molecules. The nine-coordinate strontium centers form oxygen-bridged rows [$\text{Sr}(1)–\text{Sr}(1) = 4.3870(4) \text{ \AA}$] which are linked to each other via imidazolium–carboxylate cations, as shown in Figure 4. Each strontium cation interacts with six carboxylate oxygens, stemming from four different imidazolium molecules; thus, two carboxylate groups act as chelating ligands [$\text{Sr}(1)–\text{O} = 2.688(4)–2.751(4) \text{ \AA}$], with one oxygen atom of each group further bridging adjacent strontium ions [$\text{Sr}(1)–\text{O} = 2.548(4)$ and $2.553(4) \text{ \AA}$].

The metal–organic framework in **4** is somewhat more complicated, with three independent barium, imidazolium,

- (17) For examples of Ba complexes without X-ray structures, see: (a) Perez-Inestrosa, E.; Desvergne, J.-P.; Bouas-Laurent, H.; Rayez, J.-C.; Rayez, M.-T.; Coutrai, M.; Marsau, P. *Eur. J. Org. Chem.* **2002**, 331. (b) Cacciapaglia, R.; Di Stefano, S.; Mandolini, L. *J. Org. Chem.* **2002**, 67, 521. (c) Cacciapaglia, R.; Di Stefano, S.; Mandolini, L. *J. Am. Chem. Soc.* **2003**, 125, 2224.
- (18) For examples of X-ray structures of Ca, Sr, and Ba organometallic compounds, see: (a) Izod, K.; Liddle, S. T.; Clegg, W. *J. Am. Chem. Soc.* **2003**, 125, 7534. (b) El-Kaderi, H. M.; Heeg, M. J.; Winter, C. H. *Organometallics* **2004**, 23, 4995.
- (19) For examples of X-ray structures of Ca, Sr, and Ba inorganic compounds, see: (a) Murugavel, R.; Karambelkar, V. V.; Anantharaman, G.; Walawalkar, M. G. *Inorg. Chem.* **2000**, 39, 1381. (b) Pan, Z.-Q.; Luo, Q.-H.; Duan, C.-Y.; Shen, M.-C. *Polyhedron* **2001**, 20, 2945. (c) Rossmeier, T.; Reil, M.; Korber, N. *Inorg. Chem.* **2004**, 43, 2206. (d) Hancock, R. D.; Siddons, C. J.; Reibenspies, K. J. M. *Inorg. Chim. Acta* **2004**, 357, 723. (e) Kim, Y.; Martin, S. W. *Inorg. Chem.* **2004**, 43, 2773. (f) Hamilton, B. H.; Kelly, K. A.; Malasi, W.; Ziegler, C. J. *Inorg. Chem.* **2003**, 42, 3067.

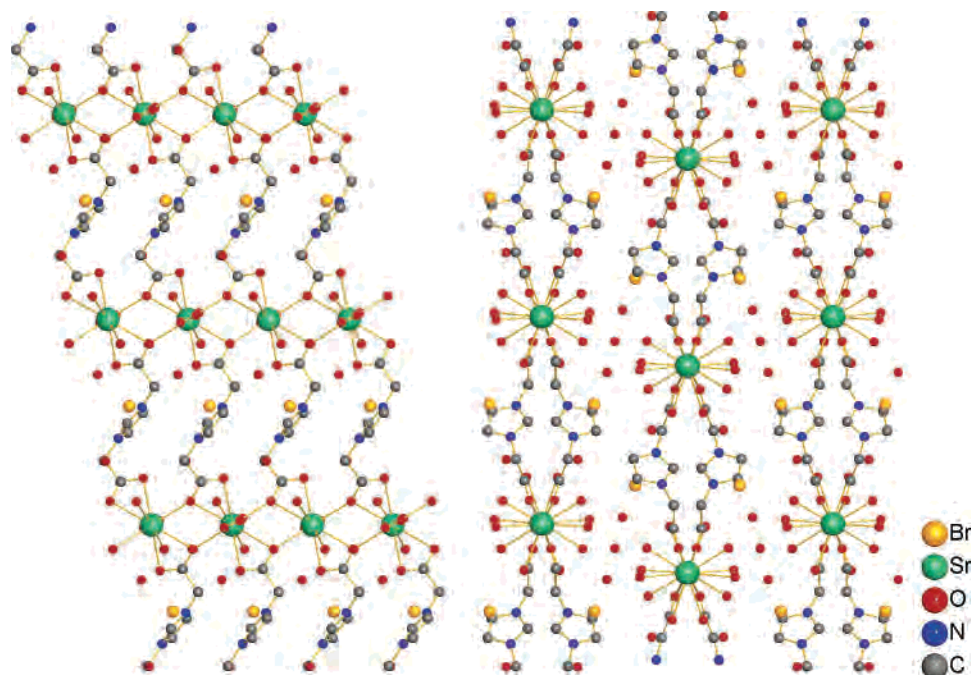


Figure 4. Crystal packing in **3** along the *b* axis (left, only one layer shown) and the *c* axis (right); hydrogen atoms have been omitted for clarity.

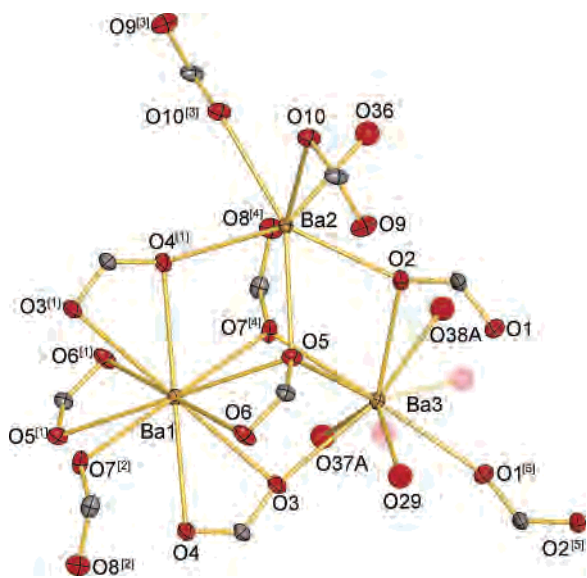


Figure 5. ORTEP plot of the coordination sphere of the Ba atoms in **4** (water oxygen atoms as balls); ellipsoids are drawn at the 50% probability level. Symmetry operations: 1 $-x, -y, 2-z$; 2 $1-x, -y, 2-z$; 3 $-x, 1-y, 2-z$; 4 $-1+x, y, z$; 5 $-x, -y, 1-z$. Selected bond lengths (Å): Ba(1)–O(3) = 2.895(4), Ba(1)–O(4) = 2.805(4), Ba(1)–O(5) = 2.827(4), Ba(1)–O(6) = 2.885(4), Ba(1)–O(7)^{2/4} = 2.867(4), Ba(2)–O(2) = 2.707(4), Ba(2)–O(4)¹ = 2.729(4), Ba(2)–O(5) = 2.792(4), Ba(2)–O(8)⁴ = 2.900(4), Ba(2)–O(10) = 2.836(4), Ba(2)–O(10)³ = 2.758(4), Ba(2)–O(36) = 2.800(5), Ba(3)–O(1)⁵ = 2.712(4), Ba(3)–O(2) = 2.758(4), Ba(3)–O(3) = 2.722(4), Ba(3)–O(5) = 2.895(4), Ba(3)–O(7)⁴ = 2.747(4), Ba(3)–O(29) = 2.791(4), Ba(3)–O(38A) = 2.867(8).

and bromine ions and approximately 9 water molecules. Crystals of **4** were markedly disordered, affecting one imidazolium ring, several water molecules, and one bromide anion. The immediate coordination sphere around the metal ions is depicted in Figure 5, with ten-coordinate Ba(1) and Ba(3) and seven-coordinate Ba(2) centers. The barium centers are connected via an extensive Ba–O network, forming BaO sheets in the crystallographic *a* axis, which

are connected to each other by two independent imidazolium moieties (Figure 6). The sheet is held together by an imidazolium moiety with a *cis* conformation, which acts as chelate ligand [via oxygen atoms O(5) and O(7)] to Ba(3), with oxygen atoms O(6) and O(8) bridging Ba(2)/Ba(3) and Ba(1)/Ba(2), respectively.

The reaction of **1** with cesium carbonate in a 1:1 molar ratio affords CsBr. However, treatment of an aqueous solution of Cs₂CO₃ with the zwitterion HA²⁰ produces **5** (empirical formula CsA·4H₂O) in a near quantitative yield. In the structure of **5** the cesium cation is surrounded by eight oxygen atoms: four originate from four different imidazolium cations and four from water (Figure 7). Distances between the oxygen atoms and the cesium ions are fairly long [3.112(4)–3.381(3) Å]. The crystal contains four water molecules per imidazolium cation, which are engaged in short hydrogen bonds to the oxygen atoms of the carboxylate moiety, with O···H distances ranging between 1.847 and 1.908 Å, as shown in Figure 7. Among the four water molecules, three are bonded to the Cs ion and one is not; it interacts with the carboxylate via hydrogen bonding instead. Thermogravimetric analysis (TGA) was carried out on **2**, **3**, **4**, and **5**. Unlike guest-free metal–organic frameworks which show high thermostability,²¹ these systems are relatively thermally unstable and begin to lose water molecules just above room temperature. For **2**, **3**, and **4**, although the coordination network of water molecules in these compounds differ, clear stepwise water loss was not observed. In each case, water loss commenced at 40 °C and continued to 200 °C, after which no further weight changes are observed, and the resulting dehydrated compounds remain stable upon

(20) The addition of a few drops of DMF is required to obtain good quality crystals; without the addition of DMF, only powders are obtained.

(21) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. Y.; Li, J. *J. Am. Chem. Soc.* **2006**, *128*, 4180.

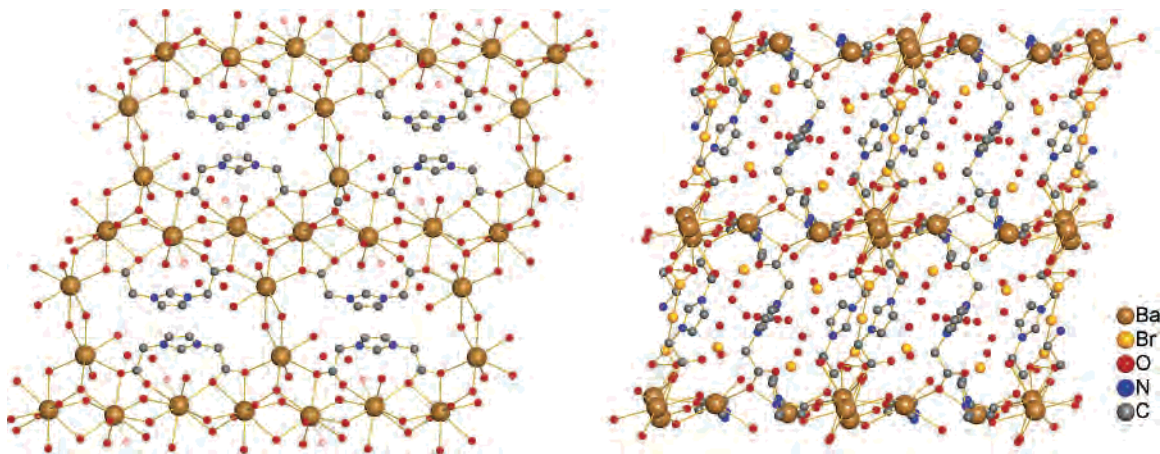


Figure 6. Ba coordination in **4** along the *a* axis (left) and packing along the *c* axis (right); hydrogen atoms have been omitted for clarity.

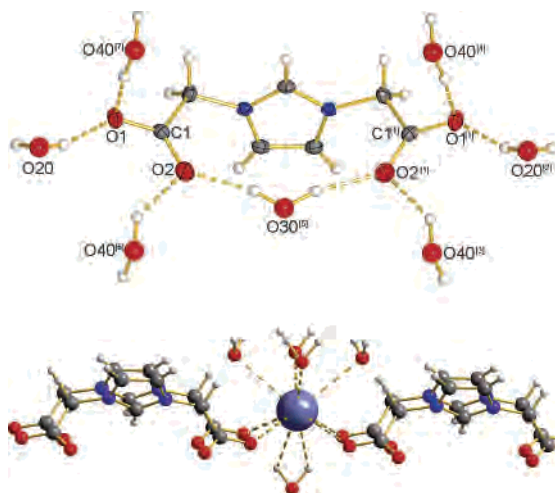


Figure 7. (top) ORTEP plot of the cation of **5** (water molecules represented as ball-and-stick figures), showing H-bonding interactions to nearby water molecules with ellipsoids drawn at the 50% probability level. Symmetry operations: [1 $1 - x, y, z$; 2 $1 + x, y, z$; 3 $1 - x, 2 - y, -0.5 + z$; 4 $1 - x, 1 - y, -0.5 + z$; 5 $x, y, -1 + z$; 6 $x, 2 - y, -0.5 + z$; 7 $x, 1 - y, -0.5 + z$. (bottom) The coordination environment about the cesium ion.

heating to 350 °C. The total water losses for compounds **2**, **3**, and **4** are in agreement with the theoretical values (obsd = 11.0, 21.5, and 15.5% versus calcd = 11.2, 22.1, and 15.8%). The water loss of **5** began at 30 °C and is complete at 180 °C, with a total of 18.1% (theoretical value 18.5%). When the compound was heated further, there was another weight loss at 290 °C, which probably is the result of the loss of CO₂ caused by the decomposition of the carboxylate groups. The thermal instability may be the result of the strong hydrogen network; all the free water molecules that are not coordinated to the metal centers form hydrogen bonds through the carboxylate, bromide, and coordinated water molecules. Thus, removal of any of the free water molecules destroys the hydrogen-bonding network and induces the collapse of the macrostructure.

Although the starting materials are closely related and the molar ratio of the acids and metal salt are the same in the reactions described above, the resulting structures of the isolated solid products are diverse. It appears that the resulting macrostructure depends markedly on the orientation of the two carboxylate moieties. In **3**, where they are *pseudo-*

trans to each other, a two-dimensional sheetlike structure is observed, whereas in **2**, where both arms point in the same direction, a three-dimensional network is obtained, as is the case when both conformations are present, as exemplified in the structure of compound **4**. In contrast to the reaction of **1** with zinc, coordination of the bromide to the metal is not observed with the “harder”, more oxophilic, alkaline earth metal centers.

Experimental Section

Acid **1** and the zwitterion [HA] were prepared according to a literature method.^{13a} Anhydrous CaCO₃, SrCO₃, BaO, and Cs₂CO₃ were from purchased Aldrich. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. ¹H NMR spectra were measured on a Bruker DMX 400, using SiMe₄ as an external standard with D₂O as the solvent. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on samples diluted in water.²² Samples were infused directly into the source at 5 μL min⁻¹ using a syringe pump, and the spray voltage was set at 5 kV with a capillary temperature of 100 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 under nitrogen on samples ranging from 5 to 10 mg at a heating rate of 5 °C/min. Elemental analysis was carried out at the EPFL.

Synthesis of 2. Acid **1** (0.265 g, 1.0 mmol) was added to a suspension of CaCO₃ (0.100 g, 1.0 mmol) in water (5.0 mL) resulting in a clear solution with concomitant evolution of CO₂. The solution was evaporated slowly at room temperature over a period of 3 days to give a white powder. The solids were filtered, washed with cold water (1.0 mL), redissolved in water, and recrystallized by slow evaporation at room temperature. This process was repeated 5 times until only crystals formed from the solution. Yield: 17%. ESI-MS: 185 [zwitterion (HA) + H]⁺. ¹H NMR (400.1 MHz, D₂O): δ 8.68 (s, 1H), 7.36 (s, 2H), 4.81 (s, 4H). ¹³C NMR (100.6 MHz, D₂O): δ 172.3, 137.1, 123.1, 51.9. IR (cm⁻¹): 3669, 3300–3400 (broad peak), 3152, 3087, 2988, 1606, 1400, 1316, 1164, 1077, 925, 794, 691, 623. Anal. Calcd for C₄₂H₅₈Br₂Ca₄N₁₂O₃₄: C, 31.63; H, 3.67; N, 10.54. Found: C, 31.66; H, 3.71; N, 10.50.

Synthesis of 3 and 4. Compounds **3** and **4** were prepared similarly by treatment of acid **1** with SrCO₃ or BaO in a 1:1 molar ratio, followed by slow evaporation at room temperature. Data for compound **3**. Yield: 98%. ESI-MS: 185 [zwitterion (HA) + H]⁺.

(22) Dyson, P. J.; McIndoe, J. S.; Zhao, D. *Chem. Commun.* **2003**, 508.

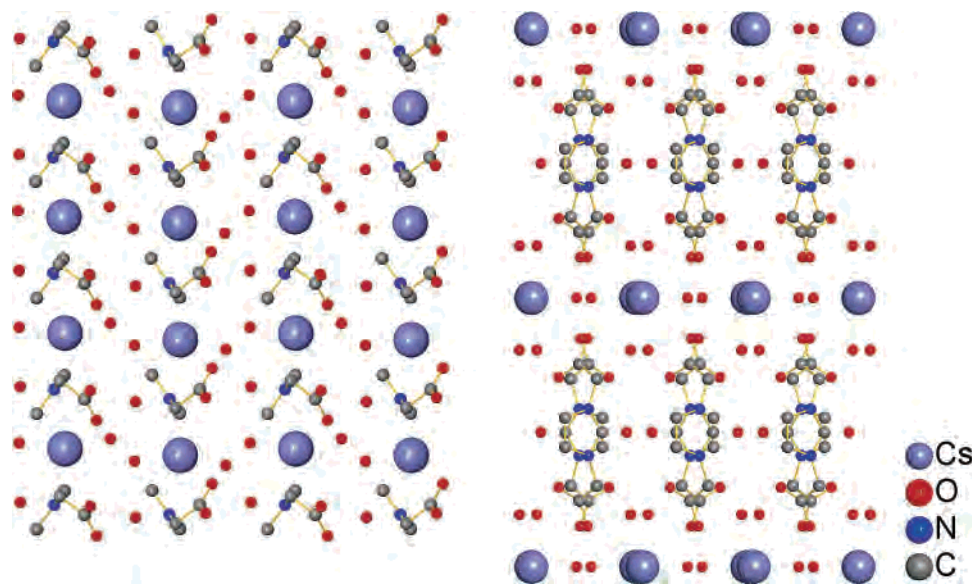


Figure 8. Crystal packing in **5** along the *b* axis (left) and the *c* axis (right); hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for **2–5**

	2	3	4	5
formula	C ₄₂ H ₆₂ Br ₂ Ca ₄ N ₁₂ O ₃₄	C ₁₄ H ₃₂ Br ₂ N ₄ O ₁₉ Sr ₂	C ₃₆ H ₃₂ Ba ₅ Br ₅ N ₁₀ O _{41.11}	C ₇ H ₁₅ CsN ₂ O ₈
<i>M</i>	1599.16	895.50	2348.73	388.12
<i>T</i> (K)	140(2)	140(2)	140(2)	140(2)
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic
space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>P1</i>	<i>Pmc2₁</i>
<i>a</i> (Å)	9.5276(10)	11.4977(9)	11.8185(7)	12.4238(10)
<i>b</i> (Å)	28.682(5)	15.7562(14)	12.3124(7)	5.1394(4)
<i>c</i> (Å)	11.657(3)	8.7724(8)	13.1178(5)	10.2685(7)
α (deg)	90.0	90.0	105.826(5)	90.0
β (deg)	90.0	101.991(7)	103.715(5)	90.0
γ (deg)	90.0	90.0	95.216(5)	90.0
<i>V</i> (Å ³)	3185.6(10)	1554.5(2)	1759.2(2)	655.65(9)
<i>Z</i>	2	2	1	2
density (Mg/m ³)	1.663	1.913	2.217	1.966
μ (mm ⁻¹)	1.696	6.082	5.697	2.858
2 θ range (deg)	2.76 \leq 2 θ \leq 25.02	2.70 \leq 2 θ \leq 25.03	3.35 \leq 2 θ \leq 25.03	3.96 \leq 2 θ \leq 25.02
reflns collected	18 687	8708	10 295	3522
independent reflns	2777 [<i>R</i> _{int} = 0.0869]	2590 [<i>R</i> _{int} = 0.0766]	5437 [<i>R</i> _{int} = 0.0277]	1041 [<i>R</i> _{int} = 0.0264]
GOF on <i>F</i> ²	1.095	1.080	1.039	1.081
final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0908, 0.2569	0.0510, 0.1304	0.0368, 0.1014	0.0159, 0.0406

¹H NMR (400.1 MHz, D₂O): δ 8.71 (s, 1H), 7.35 (s, 2H), 4.81 (s, 4H). ¹³C NMR (100.6 MHz, D₂O): δ 172.2, 137.2, 123.3, 51.8. IR (cm⁻¹): 3662, 3300–3400 (broad peaks), 3109, 3074, 2988, 2901, 1589, 1436, 1391, 1305, 1160, 1066, 973, 926, 864, 820, 788, 698, 622. Anal. Calcd for C₇H₇BrN₂O₄Sr·5.5H₂O: C, 18.82; H, 3.16; N, 6.27. Found: C, 18.86; H, 3.20; N, 6.25. Data for compound **4**. Yield: 94%. ESI-MS: 185 [zwitterion (HA) + H]⁺. ¹H NMR (400.1 MHz, D₂O): δ 8.68 (s, 1H), 7.34 (s, 2H), 4.80 (s, 4H). ¹³C NMR (100.6 MHz, D₂O): δ 172.3, 137.3, 123.1, 51.9. IR (cm⁻¹): 3665, 3360, 2988, 1593, 1434, 1394, 1305, 1168, 1066, 973, 924, 767, 699, 676, 579.

Synthesis of 5. The zwitterion [HA] (1.84 g, 10.0 mmol) was dissolved in water (5.0 mL), and Cs₂CO₃ (1.67 g, 5.0 mmol) was added at room temperature. After the mixture was stirred at room temperature for 30 min, it was concentrated to half of its original volume. DMF (0.5 mL) was added to the resulting solution, and the mixture was left at room temperature for 24 h, during which time large needles suitable for single-crystal X-ray analysis were obtained. Yield: 97%. ESI-MS: 317 [zwitterion (HA) + Cs]⁺. ¹H NMR (400.1 MHz, D₂O): δ 8.71 (s, 1H), 7.36 (s, 2H), 4.81 (s, 4H). ¹³C NMR (100.6 MHz, D₂O): δ 172.3, 137.0, 123.2, 51.8. IR (cm⁻¹): 3665, 3389, 3149, 2999, 1591, 1562, 1385, 1310, 1210,

1179, 1041, 921, 892, 790, 771, 630. Anal. Calcd for C₇H₇CsN₂O₄·4H₂O: C, 21.66; H, 3.90; N, 7.22. Found: C, 21.68; H, 3.93; N, 7.20.

Crystallography. Data collection for the X-ray structure determinations was performed on a Mar 345 diffractometer for **2** and a KUMA CCD for **3**, **4**, and **5** using graphite-monochromated Mo K α (0.71070 Å) radiation and a low-temperature device [*T* = 140(2) K]. Data reduction was performed by CrysAlis RED.²³ The structures of **2–5** were solved with SHELX97,²⁴ and that of **4** was solved with SIR-97.²⁵ The refinement was performed on PCs using the SHELX97 software package, and the graphical representations of the structures were made with ORTEP32.²⁶ The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against *F*²), and an empirical absorption correction

(23) Oxford Diffraction Ltd, Abingdon, M. P. OX14 4 RX, UK, 2003.

(24) Sheldrick, G. M. *SHELX-97, Structure Solution and Refinement Package*; Universität Göttingen: Göttingen, Germany, 1997.

(25) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(26) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Metal–Organic Frameworks

(DELABS)²⁷ was applied to all structures. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model with the exception of the H₂O hydrogen atoms, which were located on the Fourier difference map and then constrained to equal OH bond lengths and H–O–H angles, using the DFIX command implemented in SHELX. Relevant crystallographic data are compiled in Table 1. In **5**, one water oxygen was split over two positions. In **4**, there is marked disorder; bromide

Br(3), C17, O37, and O38 were split over two positions, and the DELU restraint was applied to the entire structure.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

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