Microwave-assisted synthesis of anionic metal–organic frameworks under ionothermal conditions†

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Two new isostructural coordination polymers with novel anionic metal–organic frameworks are synthesized under microwave conditions using an ionic liquid EMIm-Br as solvent and template.

The synthesis of framework materials[1,2] has attracted significant interest due to their structural diversity and vast range of potentially useful properties. Metal–organic frameworks (MOFs) are predominantly synthesized in molecular solvents under hydro(solvo)thermal conditions or *via* room temperature crystallization.[3] Ionic liquids (ILs) are catching considerable attention as greener and safer solvents due to their peculiar properties, including the lack of measurable vapour pressure and their ability to dissolve a wide range of organic and inorganic compounds.[4,5] Ionothermal synthesis,[6] using ionic liquids as the reaction media and if necessary, templates or charge-compensating groups, has been shown to be a highly promising synthetic route for a wide variety of zeolites and zeotypes.[6] Nevertheless, there are very few examples of MOFs prepared in ionic liquids,[7] and no report of anionic coordination frameworks using ionic liquids as charge-compensating structure-directing agents. Here we report the synthesis and characterization of two new anionic MOFs using an ionic liquid as both the reaction solvent and template.

Development of faster and economical routes for the synthesis of MOFs and inorganic–organic hybrid solids is an integral aspect of materials science and has been a challenging task for practical applications.[8] Generally, microwave-assisted synthesis[9] might dramatically reduce the reaction time and this simple and energy-efficient heating process has become a rapidly developing synthetic method. Although this technique is fairly common in organic synthesis[10] and has also been found to be advantageous in the preparation of inorganic materials,[11] including many zeolites, molecular sieves and nano-sized particles, very few, if any, examples of metal coordination polymers have been synthesized under microwave conditions. The characteristic properties of ionic liquids, *i.e.* high ionic conductivity and polarizability, lead them to be excellent microwave-absorbing agents and elegant solvent candidates for microwave synthesis.[12] Herein we report that under microwave or conventional ionothermal conditions, reactions of metal acetate (metal = nickel, **1** or cobalt, **2**) with trimesic acid in 1-ethyl-3-methyl imidazolium bromide (EMIm-Br, melting point

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83 °C[12]) result in the formation of novel three-dimensional (3D) anionic frameworks templated by the ionic liquid solvent.

Compound **1**, $(EMIm)_2[Ni_3(TMA)_2(OAc)_2]$, is formed phase-pure from a microwave-assisted reaction (200 °C, 50 mins) of $Ni(OAc)_2·4H_2O$ and trimesic acid in EMIm-Br. Alternatively, if a conventional ionothermal reaction in a Teflon-lined autoclave is carried out, a much longer time (180 °C, 3 days) is needed for the same phase in similar yield.‡ Comparison of powder XRD patterns of the products from these two methodologies suggested that samples prepared under microwave conditions are purer in phase and have higher crystallinity. Reactions under similar ionothermal conditions, except that $Co(OAc)_2·4H_2O$ is used instead, give $(EMIm)_2[Co_3(TMA)_2(OAc)_2]$ **2**. Single crystal X-ray diffraction confirmed that the unit cells of **1** and **2** are almost the same and powder X-ray diffraction confirms the isostructural nature of the two materials. A full single crystal diffraction study of **2** was not carried out.§

The structure of compound **1** consists of two crystallographically independent nickel atoms, Ni1 and Ni2, in distorted octahedral geometry (Fig. 1). Ni1 is chelated by two carboxylate groups from one TMA and one acetate unit, and its coordination sphere is further completed by two bis-bridging carboxylates from two different TMA ligands. Three carboxylate groups, one from acetate and the others from distinct TMAs, bridge two nickel atoms with a Ni1⋯Ni2 distance of 3.4141(4) Å. Ni2 resides on the inversion center and this generates a $Ni_3(\mu^2-\eta^1:\eta^2-CH_3COO)_2(\mu^2-RCOO)_4(chelating\text{-}RCOO)_2$[13] molecular block, which can be considered as a pseudo-octahedral secondary building unit (SBU) with four μ^2-RCOO groups on the equatorial plane and

Fig. 1 A fragment of the framework structure in **1** showing the pseudo-octahedral $Ni_3(COO)_8$ SBU: Ni—cyan; C—grey; O—red.

two *chelating*-RCOO units on the axial positions (Fig. 1). Each $Ni_3(COO)_8$ building block links, *via* the equatorial μ^2-RCOO groups, four neighboring SBUs in the crystallographic *ac* plane and therefore an infinite layer with rectangular grids of approximately 8 × 10 Å dimensions is formed. The layers are held together in an ABAB stacking sequence (Fig. 2), which reduces the openness of the network, because the axial *chelating*-RCOO ligands act as pillars to form a three-dimensional (3D) anionic framework. The whole network can be described as a (3,6)-connected net by the packing of octahedral $[Ni_3(COO)_8]_6$ building units and TMA ligands as 6- and 3-connecting topological nodes respectively. The overall (3,6)-connected net can be further specified by the Schläfli symbol $(6^3)(6^{12}.8^3)$ where the shortest rings meeting at the twelve and three angles of the 6-connected vertices are 6- and 8-membered respectively while those at the three angles of 3-connected vertices are 6-membered.[14]

The cage within the octahedral $[Ni_3(COO)_8]_6$ building unit is large enough to encapsulate two $(EMIm)^+$ cations per pore (Fig. 2). It should be noted at this point that the $(EMIm)^+$ cations not only adopt a charge-compensating and space-filling role in the material, but also direct the formation of the host framework, since the reactions of nickel acetate with trimesic acid in some other ionic liquids, such as 1-butyl-3-methyl imidazolium bromide, or eutectic mixtures give rise to different phases of products. Further study on MOFs using various ionic liquids as templates is now in process.

The simulated X-ray powder diffractograms of compounds **1** and **2** compare well with those measured for the bulk samples. Thermogravimetric analysis of **1** and **2** under a nitrogen atmosphere showed a slightly decreasing plateau ($<\sim 1.5\%$ weight loss) until 300 °C, where the compounds began to decompose, suggesting that they might have considerable physical thermal stability. The utility of MOFs as porous solids depends on being able to remove the guest cations without destroying the frameworks, which cannot be done thermally in this case, and so the networks are not porous. Furthermore, it is remarkable that though **1** and **2** are insoluble in methanol, they dissolve in aqueous
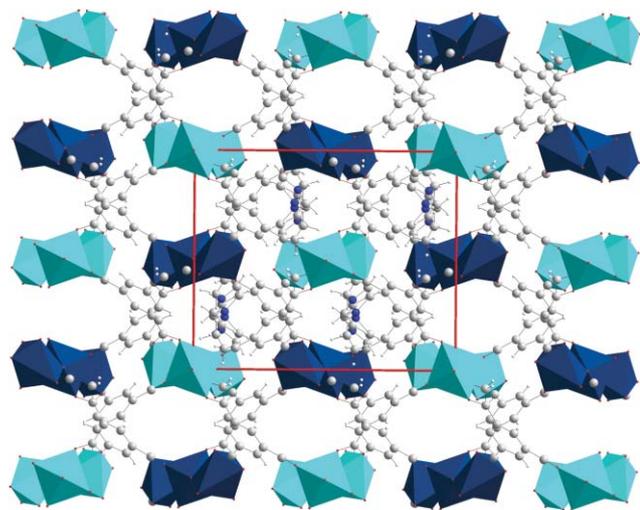
solutions immediately and give pale green and pink precipitates, respectively.

In summary we present here the first anionic coordination frameworks from an ionic liquid under microwave conditions. The ionothermal approach opens up new possibilities for the preparation of MOFs and many previously unknown materials. The use of the microwave technique reported suggests a simple yet highly efficient way for the synthesis and crystallization of new MOFs and functional materials.

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Fig. 2 A view of the 3D network composed of $Ni_3(COO)_8$ SBUs in an ABAB stacking sequence in **1** along the *b*-axis. Ni in A or B layer—cyan and blue polyhedra; C—grey ball; N—blue ball. $(EMIm)^+$ cations outside the unit cell are omitted.

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