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Two-dimensional anionic zinc benzenedicarboxylates: Ionothermal syntheses, structures, properties and structural transformation

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ABSTRACT

The ionothermal synthesis of two intercalated two-dimensional zinc benzenedicarboxylates, $EMIm_2[Zn_3(C_6H_4(COO)_2)_3Cl_2]$ (**I**) and $BMIm_2[Zn_3(C_6H_4(COO)_2)_3Cl_2]$ (**II**), employing the ionic liquids 1-ethyl-3-methylimidazolium chloride (EMIm-Cl) and 1-butyl-3-methylimidazolium chloride (BMIm-Cl) as solvents, is reported. Detailed characterization by X-ray diffraction, elemental analyses, vibrational and optical spectroscopies, and thermogravimetric analysis is described. The two compounds display an anionic two-dimensional structure with the composition $[Zn_3(C_6H_4(COO)_2)_3Cl_2]^{2-}$ which is intercalated and charge neutralized by the imidazolium cations. The compounds are remarkably stable: neither begins to lose mass until they are heated above 300 °C, above which temperature ZnO is obtained. The structural transformation of the anionic layered compounds **I** and **II** to a neutral one-dimensional structure with the composition $Zn(C_6H_4(COO)_2)(H_2O)_2$ is described. The derived neutral compound shows better thermal robustness. Both the parent and the transformed structures display blue luminescence, arising from ligand centered $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

1. Introduction

The continuous growth of interest in coordination polymers stems not only from potential applications in areas such as selective gas storage/adsorption, catalysis and luminescence, but also from their intriguing structures and topologies [1–8]. Although the coordination of ligands to central metal ions and the ultimate assembly of building units in the solid state can be accomplished in numerous ways, one of the most frequently employed synthetic routes is the solvo(hydro)thermal technique [2,3]. However, there are some possible drawbacks to this approach such as the potential for unwanted side reactions, for example, in the hydrolysis of organic ligands the incorporation of water or solvent in the final product, or other problems associated with the very poor solubility of the reactants [9,10]. The ionothermal technique, which involves the use of ionic liquids as solvents, *e.g.* 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIm-BF_4$), 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMIm-PF_6$) and 1-ethyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]amide ($BMIm-Tf_2N$), at lower vapor pressures and near-ambient temperatures, has recently emerged as a promising green alternative [10–14]. This is an attractive approach because small changes to the nature of the cationic and/or anionic components of ionic liquids give rise to well-determined changes in their properties, such as polarity, ionic conductivity and vapor pressure [11–16]. This degree of control makes them suitable to be solvents for a wide range of precursors. The possibility of ionic liquids becoming incorporated into the products as ligands, charge compensating motifs and even templates for open frameworks, make them functional solvents in syntheses [11–16]. In the synthesis of coordination polymers, dicarboxylate ligands have been extensively investigated as framework building units [17–20], particularly notable are Zn-benzenedicarboxylate compounds [18–20]. This family of compounds are nonetheless very sensitive to variations in the synthetic conditions, including type of solvent and the water content in the reactions. The use of ionic liquids is therefore very interesting in providing a polar non-aqueous system.

In the work described here, we employed two ionic liquids, 1-ethyl-3-methylimidazolium chloride (EMIm-Cl) and 1-butyl-3-methylimidazolium chloride (BMIm-Cl) (Scheme 1) as functional solvents for the synthesis of two intercalated two-dimensional frameworks, $EMIm_2[Zn_3(BDC)_3Cl_2]$ (**I**) and $BMIm_2[Zn_3(BDC)_3Cl_2]$ (**II**) (H_2BDC = 1,4-benzenedicarboxylic acid). The effect of the intercalated ionic liquids on the derived framework structures, supramolecular assemblies and topologies is discussed. A study on the structural transfromation of compounds **I** and **II** after the removal of the intercalated ionic liquids by leaching in warm water is described. The vibrational spectroscopic, thermogravimetric and photoluminescence properties of compounds **I** and **II** and the corresponding structures after the transformation are reported.

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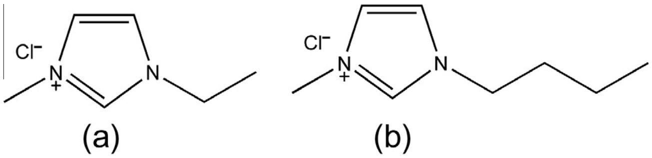

Scheme 1. Schematic illustrations of the ionic liquid solvents: (a) 1-ethyl-3-methylimidazolium chloride (EMIm-Cl) and (b) 1-butyl-3-methylimidazolium chloride (BMIm-Cl).

2. Experimental

2.1. Materials and methods

All chemicals were obtained commercially and used without further purification: $Zn(NO_3)_2{\cdot}6H_2O$ (98% Ajax Finechem), 1,4-benzenedicarboxylic acid (H_2BDC; $C_6H_4(COOH)_2$, 97% BDH), 1-ethyl-3-methylimidazolium chloride (EMIm-Cl; $C_6H_{11}ClN_2$; 99% Sigma–Aldrich) and 1-butyl-3-methylimidazolium chloride (BMIm-Cl; $C_8H_{15}ClN_2$; 99% Sigma–Aldrich).

Infrared (IR) spectra were recorded using a Bruker Tensor 27 FT-IR instrument in the range 400–4000 cm^{-1} using KBr discs (98.5% BDH). Raman spectra were collected in the range 100–4000 cm^{-1} using a JOBIN YVON HORIBA T64000 spectrophotometer, operated with a 35 mW solid state laser excitation source. UV–Vis spectra were collected on a suspension of ground samples in deionised water at room temperature from 200 to 800 nm using a Perkin Elmer UV LAMDA 25 spectrophotometer. Photoluminescence spectra were collected at room temperature using an Avantes Multichannel spectrometer with an Ocean Optics LED 255 nm excitation source. Thermogravimetric analyses were performed on a SDT Q600 V20.9 Build 20 from room temperature to 900 °C with a heating rate 10 °C min^{-1} in a nitrogen gas flow. X-ray powder diffraction experiments were conducted using a Rigaku MiniFlex II desktop X-ray diffractometer operated with Cu Kα radiation (λ = 1.5418 Å).

2.2. Syntheses of $EMIm_2[Zn_3(BDC)_3Cl_2]$ (*I*) and $BMIm_2[Zn_3(BDC)_3Cl_2]$ (*II*)

Single crystals of $EMIm_2[Zn_3(BDC)_3Cl_2]$ (**I**) and $BMIm_2[Zn_3(BDC)_3Cl_2]$ (**II**) were synthesized from the reactions between $Zn(NO_3)_2{\cdot}6H_2O$ (0.7437 g, 2.5 mmol) and H_2BDC (0.0856 g, 0.5 mmol) in EMIm-Cl (1.0000 g, 6.8 mmol) for **I** and in BMIm-Cl (1.0000 g, 5.7 mmol) for **II**. The reactions were performed at 180 °C for 10 days, using a 7.00 mL Teflon autoclave. Optical microscopy showed each sample contained colorless crystals with well-defined faces. It may be noted that the mole ratio of $Zn(NO_3)_2{\cdot}6H_2O{:}H_2BDC$ was varied from 3:1 to 6:1, but only the ratio of 5:1, as described above, afforded crystals of the product. The other ratios resulted in a viscous brown solution without any solid products. The X-ray powder diffraction data confirmed the purity of the bulk crystalline products. *Anal.* Calc. for $Zn_3C_{36}H_{34}N_4O_{12}Cl_2$ (**I**): C, 44.01; H, 3.46; N, 5.70. Found: C, 43.88; H, 3.47; N, 5.82%. *Anal.* Calc. for $Zn_3C_{40}H_{42}N_4O_{12}Cl_2$ (**II**): C, 46.25; H, 4.08; N, 5.40. Found: C, 46.29; H, 4.12; N, 5.45%.

2.3. Single crystal structure determinations

Single crystal X-ray diffraction data from **I** and **II** were collected from crystals of the size 1.00 × 0.90 × 0.40 and 0.70 × 0.38 × 0.20 mm, respectively, at 293(2) K using a Bruker APEX-II CCD diffractometer operated with Mo K radiation (= 0.71073 Å). Data reduction and a numerical absorption correction were performed with the SAINT [21] and SADABS [22] software packages. The structures were solved by direct methods implemented within SHELXS-86 [23] and full-matrix least squares refinements were carried out against F^2 for all data with the program SHELX-97 [23] *via* the WinGX [24] program interface.

Due to a twinning problem in the case of **II**, another set of diffraction data was collected at 150(2) K on a crystal of size 0.33 × 0.13 × 0.13 mm, using a Stöe IPDS2 image plate diffractometer and Mo Kα radiation. The collected data were analytically corrected for absorption using the Tompa method [25]. Both data sets of **II** show twinning problems and refinements employed the HKLF5 formalism to include data from both twin domains. For the data collected at 293(2) K, the twin law (1 0.025 0.033, 0-1 0, 0 0-1), which was determined by Rotax [26], was used. This twin law mimics the higher Laue group (2/*m*). In the final refinement the two twin components were present in the ratio 0.782:0.218(2). Treatment with Rotax and refinement using data from both twin domains resulted in an improvement of the R and wR_2 values from 0.0769 and 0.2278 to 0.0590 and 0.1639, respectively. Approximately 6% of the data, suspected to be partially overlapped, was omitted. For the 150(2) K data set, there was no evidence of pseudomerohedral twinning to mimic the higher Laue group. The crystal examined was found to be non-merohedrally twinned. Both twin components were integrated and used in refinements (HKLF5).

2.4. De-intercalation and structural transformation of *I* and *II*

In order to study the structures and properties of the de-intercalated samples of **I** and **II**, the crystals were dispersed in deionised water at 70(5) °C for 60 min, using a general ultrasonic bath. Fine white powders were obtained after ultrasonication for both compounds, and were characterized by elemental analyses, X-ray powder diffraction, IR and Raman spectroscopies, thermogravimetric analyses, UV–Vis and photoluminescence spectroscopies.

3. Results and discussion

3.1. Description of the crystal structures

Compounds **I** and **II** feature topologically identical two-dimensional $[Zn_3(BDC)_3Cl_2]^{2-}$ anionic layers which are intercalated and charge-neutralized by different extra-framework cations, *i.e.* $EMIm^+$ (**I**) and $BMIm^+$ (**II**) (Scheme 1). The crystallographic data and refinement details for **I** and **II** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3.1.1. $EMIm_2[Zn_3(BDC)_3Cl_2]$ (*I*)

As depicted in Fig. 1a, the asymmetric unit of **I** contains twenty-nine non-hydrogen atoms, comprising two crystallographically independent Zn ions (Zn1 and Zn2), one and a half molecules of BDC^{2-}, a single chloride anion and a single $EMIm^+$ cation. The four-coordinated Zn1 shows a tetrahedral environment fulfilled by an apical Cl^- anion and three basal O atoms (O1, O3, O5). The six-coordinated Zn2, on the other hand, shows a regular octahedral geometry completed by two equivalent apical O atoms (O5) and two pairs of equivalent O atoms (O2 and O4) in a square plane. The tetrahedral and octahedral units of Zn ions share a common vertex (O5). The Zn–O bond distances of the tetrahedral Zn1 (1.955(5)–1.972(4) Å) and the octahedral Zn2 (2.028(5)–2.195(4) Å) are in good agreement with those reported for similar compounds [27–30].

The Zn1 and Zn2 ions are linked through two μ_2–$\eta^1{:}\eta^1$ carboxylato bridges (O1–C7–O2 and O3–C8–O4) of two equivalent BDC^{2-} ligands, and an μ_2–$\eta^2{:}\eta^0$ carboxylato bridge (O5 of O5–C12–O6) of the other BDC^{2-} ligand. The inversion centre located