**Ionothermal synthesis of 3d–4f and 4f layered anionic metal–organic frameworks†**

Wen-Xian Chen, Yan-Ping Ren,* La-Sheng Long,* Rong-Bin Huang and Lan-Sun Zheng

Received 22nd January 2009, Accepted 24th April 2009

First published as an Advance Article on the web 21st May 2009

DOI: 10.1039/b901404g

A La(III)–Co(II) heterometallic framework and a La(III)-based anionic layered architecture were prepared under ionothermal conditions.

Ionic liquids (ILs), a class of organic solvents, have received much attention recently due to their peculiar properties, including unusually low melting points, nonvolatilility, nonflammability, thermally stability, recycle and versatile ability to dissolve many substances.1,2 Normally, ILs are highly studied in separations, electrochemistry, lubrications, life sciences, and catalytically active solvents for synthetic chemistry, etc.3 Recently, based on their unique properties, ILs have been explored and utilized in the areas of zeotypes preparation and synthetic coordination chemistry.4,5 Distinguishing from traditional hydro/solvothermal syntheses which are frequently stratagies to construction of coordination polymers,6,7 ionothermal synthesis is of particular interest, in which ionic liquids participate as both solvent and structure-directing agent, resulting in interesting anionic metal–organic frameworks.8 It is worth noting that ionothermal synthesis of metal–organic frameworks, while very common in transition-metal-based coordination polymers,9 is almost absent in the construction of 3d–4f or 4f coordination structures up to date, despite the effort made in this field.10 We report the ionothermal synthesis of two lanthanide-based frameworks, namely, [La2Co(nipt)2(CH3COO)2(CH3SO3)4][EMIm]+, 1 and [La(nip)BrCl][EMIm]− (2).

The one-pot reaction of 5-methylisophthalic acid (H2mipt), LaCl3·nH2O and Co(OOCCH3)2·4H2O in ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate (EMIm-MSul) resulted in pink crystals of 1.† Fig. 1a shows the coordination environment of La(III) and Co(II) in 1. The structure of 1† features a layered La(III)–Co(II) heterometallic anionic open framework which is made up of infinite La(III)–Co(II) chains connected by mipt ligands. The coordination environment around the Co(II) ion, located in hexa-coordinated octahedron geometry, is coordinated by two mipt ligands, two CH3COO− anions and two CH3SO3− anions. The Co–O distances, ranging from 2.067(4) to 2.149(4) Å, are in agreement with those observed for the hexa-coordinated Co atom in carboxylate complexes.11 In 1, the central La(III) ion is ligated by three monodentate CH3SO3− anions, one monodentate CH3COO− anion, one bidentate CH3COO− anion, one bidentate carboxylate and one monodentate carboxylate, respectively, from two different mipt ligands in a capped square antiprism coordination geometry. The La–O distances range from 2.421(4) to 2.706(4) Å, compared to those of 2.398(3)–2.678(3) Å in the nona-coordinated La(III)-complex.12 Two La(III) centers linked, respectively, through a pair of CH3COO− anions and CH3SO3− anions, result in a dinuclear unit. The connection of adjacent dinuclear units through CoO6 anion in 1, one carboxylate coordinating with one La(III) ion from one neighboring chain in chelating mode, and another carboxylate bridging one La(III) and one Co(II) from another neighboring chain in syn–syn bridging mode, leading to a 2D anionic network. EMIm cations acting as guests and encounter ions, located in the hydrophobic cavity of 1 as illustrated in Fig. 2b, while the anionic component CH3SO3− ions of the ionic liquid are coordinated with the La(III) ion in 1.

Mixing 5-nitroisophthalic acid (H2nip), LaCl3·nH2O in ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIm-Br) through ionothermal reaction results in colorless needle crystals of 2.†

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† Electronic supplementary information (ESI) available: TG analysis for compounds 1 and 2 (Fig. S1–S2); IR spectra for compounds 1 and 2 (Fig. S3–S4); CCDC reference numbers 717557 and 717558. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901404g

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**Fig. 1** ORTEP plot showing (a) the coordination environment of La(III) and Co(II) ions in 1. Symmetry codes: A −x + 1, −y + 2, −z + 1; B −x + 1, −y + 2, −z + 2; C x, y, z − 1; D −x, −y + 2, −z + 2; E x − 1, y, z; F −x, −y + 2, −z + 1. (b) The coordination environment of La(III) ion in 2. Symmetry codes: A −x + 1/2, y, z + 1/2; B x, y − 1, z; C −x + 1/2, y − 1, z + 1/2.
Single-crystal analysis reveals that 2 is crystallized in the orthorhombic system, space group Pca21. Fig. 1b shows the coordination environment of La(III) in 2. The central La(III) ion is nona-coordinated by one bromine anion, two chlorine anions, two chelate carboxylates and two monodentate carboxylates, respectively, from four nip ligands in a capped square antiprism environment. The bond lengths of La–O, La–Cl and La–Br are 2.496(7)–2.733(8) Å, 2.848(3)–2.877(3) Å, and 2.943(2) Å, within the expected ranges reported for La(III) complexes.13

Crystal structure analysis reveals that 2 exhibits a layered anionic framework consisting of 1D chains similar to that in 1. In contrast to the La(III)–Co(II) chains in 1, the 1D chains in 2 are composed entirely of La(III) ions, connected by chlorine anions and carboxylate oxygens of nip ligands as shown in Fig. 3a. The nip ligand connects adjacent 1D chains through its one carboxylate bridging two La(III) ions from one neighboring chain in chelating/bridging mode, and another carboxylate also bridging two La(III) ions from another neighboring chain in the same coordination mode, producing a 2D network as shown in Fig. 3b. The void space of the 2D anionic network is occupied by the EMIm cations.14

Thermogravimetric analysis shows that compound 1 has no weight loss before 265 °C in air (see Fig. S1†). Between 265 and 435 °C, compound 1 undergoes weight loss in two steps. The first weight loss covered a temperature range from 265 to 435 °C, the weight loss of 40.3% corresponds to loss of EMIm cations and mpht ligands (41.2%). The second weight loss covered a temperature range from 435 to 600 °C, the weight loss of 15.4% corresponds to the removal of the CH3COO− ligands and the CH3SO3− ligands. Thermogravimetric analyses shows that compound 2 has no weight loss before 280 °C (see Fig S2†). The organic contents begin to be lost in continuous steps until about 550 °C. The total weight loss of 62.8% corresponds to the loss of the EMIm cations, the chlorine and the nip ligands (calc 62.2%).

In summary, we have reported two lanthanide-involved layered anionic metal–organic frameworks synthesized through ionothermal reaction. We reveal that the structure of the Ln(III)-based coordination polymer obtained from ionothermal synthesis often exhibits different structural patterns from those obtained using a routine synthetic approach, due to lacking of the coordination of water (or solvent) to Ln(III) center. Thus, the present work demonstrates that ionothermal synthesis is an efficient synthetic approach to new lanthanide-based coordination materials.
Compound 1 was synthesized as follows: 0.353 g LaCl₃·nH₂O, 0.249 g Co(OOCCH₃)₂·4H₂O and 0.180 g 5-methylisophthalic acid were mixed in 1.3 mL 1-ethyl-3-methyl imidazolium methanesulfonate. Then the mixture was subsequently sealed to a 25 mL Teflon-lined Parr at 140 °C for about a week and cooled to room temperature at the rate of 3 °C/h. The pink crystals were obtained with 21.7% yield (based on LaCl₃·nH₂O). Anal. Calcd. (Found) for LaCl₃·nH₂O, 0.211 g 5-nitroisophthalic acid and 1.2 g ionic liquid 1-ethyl-3-methyl imidazolium bromide was sealed to a 25 mL Teflon-lined Parr at 160 °C for about a week and cooled to room temperature at the rate of 3 °C/h. The pink crystals were obtained with 21.7% yield (based on LaCl₃·nH₂O). Anal. Calcd. (Found) for C₃₈H₅₂N₄O₂₄S₄La₂Co (KBr, cm⁻¹): C, 29.24(29.21); N, 7.31(7.21); H, 2.44(2.83). IR Spectra for 1: 3432.22(s), 1620.55(s), 1543.10(s), 1382.38(s), 1455.15(s), 1351.33(m), 1349.72(m), 1165.54(m), 725.17(m), 1090.77(w), 790.99(w), 524.02(w).

Compound 2 was ionothermal synthesized as follows: a mixture of 0.353 g LaCl₃·nH₂O, 0.211 g 5-nitroisophthalic acid and 1.2 g ionic liquid 1-ethyl-3-methyl imidazolium bromide was sealed to a 25 mL Teflon-lined Parr at 140 °C for about a week and then cooled to room temperature at the rate of 3 °C/h. The colorless crystals were obtained with 30.4% yield (based on LaCl₃·nH₂O). Anal. Calcd. (Found) for C₄₁H₄₆N₉O₆ClBrLa₂, 0.180 g 5-methylisophthalic acid and 1.2 g ionic liquid 1-ethyl-3-methyl imidazolium methanesulfonate. Then the mixture was subsequently sealed to a 25 mL Teflon-lined Parr at 160 °C for about a week and then cooled to room temperature at the rate of 3 °C/h. The pink crystals were obtained with 30.4% yield (based on LaCl₃·nH₂O). Anal. Calcd. (Found) for C₃₈H₅₂O₂₄N₄S₄La₂Co (KBr, cm⁻¹): C, 29.24(29.21); N, 7.31(7.21); H, 2.44(2.83). IR Spectra for 2: 3432.22(s), 1620.55(s), 1543.10(s), 1382.38(s), 1455.15(s), 1351.33(m), 1349.72(m), 1165.54(m), 725.17(m), 1090.77(w), 790.99(w), 524.02(w).