

## [Cu(I)(bpp)]BF<sub>4</sub>: the first extended coordination network prepared solvothermally in an ionic liquid solvent

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Received (in Columbia, MO, USA) 11th June 2002, Accepted 9th October 2002

First published as an Advance Article on the web 31st October 2002

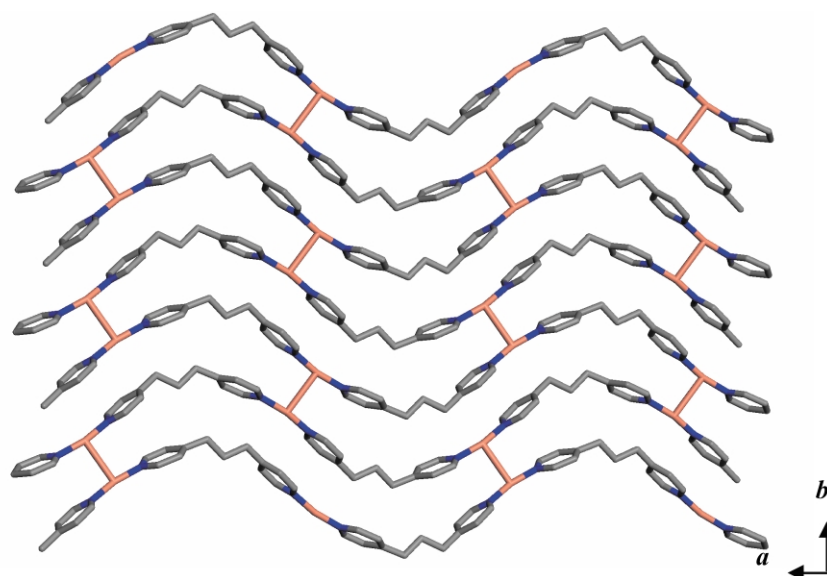
Use of an ionic liquid [bmim][BF<sub>4</sub>] (bmim = 1-butyl-3-methylimidazolium) as solvent has resulted in the first extended coordination structure, the two-dimensional network [Cu(bpp)]BF<sub>4</sub> [bpp = 1,3-bis(4-pyridyl)propane], produced *via* a solvothermal route.

In the past few years, room temperature ionic liquids (RTILs), especially those based on noncoordinating dialkylimidazolium cations with poorly coordinating anions, have been studied extensively as promising solvent candidates for clean technologies.<sup>1</sup> While admirable progress has been made in exploring their applications as green solvents in organic synthesis and catalysis,<sup>2</sup> they have been utilized little in the areas of synthetic coordination chemistry.<sup>3</sup> To this date, no extended coordination structures have been synthesized in a RTIL. In this communication, we report our strategy and rationale in the solvothermal synthesis of coordination polymers using 1-butyl-3-methylimidazolium tetrafluoroborate as a solvent and the first coordination network structure, [Cu(I)(bpp)]BF<sub>4</sub>, prepared solvothermally in [bmim][BF<sub>4</sub>] from a Cu(II) salt and 1,3-bis(4-pyridyl)propane (bpp) ligand.

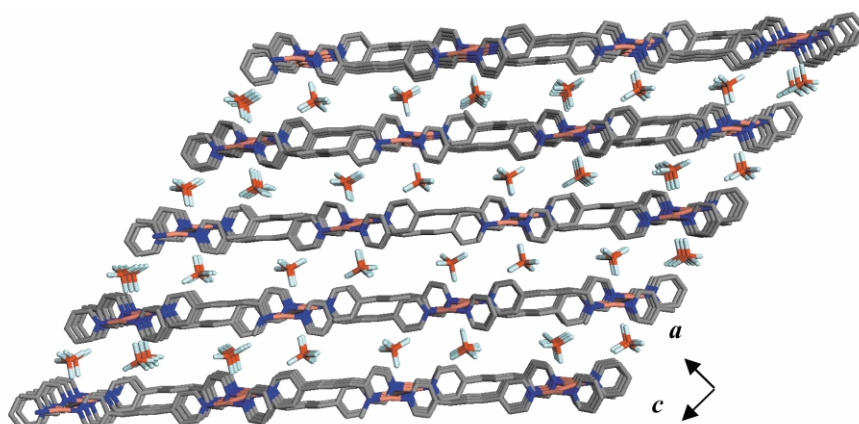
[bmim][BF<sub>4</sub>], as a room temperature ionic liquid, is air and moisture stable, neutral, non-volatile, and weakly coordinating.<sup>4</sup> With a high thermal stability, it remains intact upon heating to 400 °C. In addition, both its cation and anion can serve as templates or charge compensating groups in the synthesis. These properties make it ideal as a green reaction medium for use in the solvothermal reactions.<sup>5</sup> Reactions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O with bpp in [bmim][BF<sub>4</sub>] yielded a Cu(I)-bpp coordination polymer, [Cu(bpp)]BF<sub>4</sub> **1**.<sup>†</sup> The BF<sub>4</sub><sup>-</sup> anions entered the final structure as a charge compensating species. Solvent incorporation behaviour has been observed in many

previous solvothermal processes, including a number of reactions utilizing amines and diamines as solvents.<sup>6</sup> Note the reduction of Cu(II) to Cu(I) in the formation of **1**. Such a process has been commonly observed under hydro(solvo)thermal conditions with amine or pyridine containing ligands.<sup>7</sup>

The crystal structure of **1**, shown in Fig. 1 and Fig. 2, was determined by the single crystal X-ray diffraction method.<sup>‡</sup> Each Cu(I) ion is coordinated to two nitrogen atoms from separate bpp ligands giving rise to a wave-like Cu-bpp chain which extends into a two dimensional framework *via* weak inter-chain interactions of copper pairs. The Cu(I)-Cu(I) weak interactions have been reported previously, and the Cu(I)-Cu(I) distance of 3.002(2) Å in the title compound is comparable to those found in [Cu<sub>4</sub>(2-(3(5)-pz)-6-mepy)<sub>4</sub>]<sub>2</sub>·3tol {py = pyridine, pz = pyrazolyl, tol = toluene} and in [CuL][CuCl<sub>2</sub>] {L = 1,1'-bis(2-pyridyl) octamethylferrocene}, where Cu(I) atoms have a similar coordination environment.<sup>8</sup> Topologically, this 2D network can be regarded as a wavelike brick wall.<sup>9</sup> The BF<sub>4</sub><sup>-</sup> anions occupy the space between the 2D layers. Among numerous known structures containing the flexible ligand bpp, the similar wavelike chains have been found in the [Ag(bpp)](CF<sub>3</sub>SO<sub>3</sub>)·EtOH and [Ag(bpp)]NO<sub>3</sub> structures<sup>10</sup> but the metal-metal interactions are quite different in these compounds. [Ag(bpp)]PF<sub>6</sub> is the only structure found similar to **1**, which was prepared by slow diffusion using silver perchlorate in methanol solution.<sup>11</sup> The weak Ag-Ag bond is 3.0852(9) Å in [Ag(bpp)]PF<sub>6</sub>. All other known Cu-bpp compounds contain Cu(II), and have been prepared *via* different solution routes and have different structures from the brick-wall network of **1**. For example, [Cu(bpp)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]·0.25H<sub>2</sub>O and [Cu(bpp)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] were obtained from ethanol-water solutions at room temperature.<sup>12</sup> In both structures, the Cu ions are four-



**Fig. 1** A view of **1** along the crystallographic *c*-axis showing a single layer of [Cu(bpp)]<sup>+</sup>. Copper atoms and Cu-Cu bonds are in orange, carbon and nitrogen atoms are in grey and blue, respectively. Selected bond distances and angle: Cu-N1 1.884(4), Cu-N2i 1.885(4) Å, N1-Cu-N2i 167.43(19)° (symmetry code: i 1 + x, ½ - y, ½ + z).



**Fig. 2** A view of **1** along the crystallographic *b*-axis showing parallel-stacked [Cu(bpp)]<sup>+</sup> layers and BF<sub>4</sub><sup>-</sup> anions located between these layers. Boron atoms are in red and fluorine atoms, in light-blue.

coordinated to bpp ligands and have a 2D grid-like network. In a similar way, {[Cu<sub>5</sub>(bpp)<sub>8</sub>(SO<sub>4</sub>)<sub>4</sub>(EtOH)(H<sub>2</sub>O)<sub>5</sub>](SO<sub>4</sub>)}·EtOH·25.5H<sub>2</sub>O was crystallized by slow diffusion of the ligand in an ethanolic solution into aqueous copper(II) salt solution.<sup>13</sup> The structure of this compound is a 3D network composed of a 1D motif and a grid-like 2D motif. Employing a room temperature diffusion method similar to that used to prepare [Ag(bpp)]PF<sub>6</sub> did not produce **1**. Clearly, the formation of **1** is sensitive to the experimental conditions.

In summary, we have explored the use of an ionic liquid [bmim][BF<sub>4</sub>] as a thermally stable and poorly coordinating solvent in the solvothermal synthesis of the coordination polymer [Cu(I)(bpp)]BF<sub>4</sub> **1**. The structure of **1** is different from those obtained *via* other routes such as diffusion or solution synthesis. This study demonstrates that ionic liquids, with their superior properties, may be promising for use as a new type of clean and effective solvent in the preparation and crystallization of coordination polymers.

## Notes and references

† [bmim]Cl was prepared from 1-methyl imidazole and chlorobutane, recrystallized until colorless from ethyl acetate–acetonitrile, and then converted to [bmim]BF<sub>4</sub> using NH<sub>4</sub>BF<sub>4</sub> in acetone by adaptation of literature procedures.<sup>14</sup> A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.05 mmol) and bpp (0.05 mmol) in [bmim][BF<sub>4</sub>] (0.1 ml) was sealed in a glass tube under vacuum. The reaction was carried out at 140 °C for 3 days. The product was cooled naturally to room temperature. It was filtered and washed with distilled water and then 30% and 70% ethanol followed by drying with anhydrous diethyl ether. Column-like orange crystals were collected.

‡ Crystal data of **1**: C<sub>13</sub>H<sub>14</sub>BCuF<sub>4</sub>N<sub>2</sub>, *M* = 348.61, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 10.451(2), *b* = 8.557(2), *c* = 16.569(3) Å, β = 95.50(3)°, *V* = 1474.9(5) Å<sup>3</sup>, *D*<sub>c</sub> = 1.570 g cm<sup>-3</sup>, *T* = 293(2) K, μ(Mo-Kα) = 1.516 mm<sup>-1</sup>. 8887 reflections measured, 2699 unique (*R*<sub>int</sub> = 0.050), *R* = 0.0643, *wR* = 0.1257 for 2049 observed reflections (*I* > 2σ(*I*)). CCDC 187373. See <http://www.rsc.org/suppdata/cc/b2/b209937n/> for crystallographic data in CIF or other electronic format.

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