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Room-Temperature Ionic Liquids: For a Difference in the Supramolecular Synthesis

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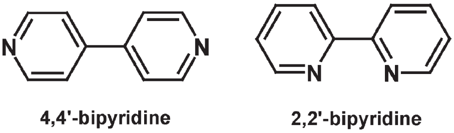
Summary: Cu(I) and Ni(II) coordination polymers with 4,4′-bipyridine and 2,2′-bipyridine, respectively, that have been synthesized from an ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) gave different coordination environment and supramolecular networks than the corresponding synthesis from the other solvents. The resultant complexes were characterized by single crystal x-ray diffraction methods.

Keywords: ionic liquids; supramolecular

Introduction

Supramolecular synthesis of molecular complexes, assemblies, adducts, etc., using organic or mixture of organic and inorganic substrates, are in general performed by employing (volatile) organic solvents following the procedure popularly known as co-crystallization.[1–8] From the literature, a significant correlation between the subtle variations in the ultimate topology of the assembly being formed and the change of medium of crystallization is known.[9–14] In particular, in the case of coordination polymers, effect of such variations is predominant with remarkable changes in the coordination of metal ions and the resultant three-dimensional arrangement of the species. In this respect, in agreement with the previous reports,[12–14] we too have recently demonstrated the formation of different types of networks by Co(II) complexes of 3,5-dinitrobenzoate and its analogues by crystallizing from different organic solvents.[15]

Of late, an increased awareness for pollution-free environment reinforced a search for alternative strategies for the synthesis of molecular or supramolecular compounds avoiding toxic chemicals like organic solvents.[16–19] Thus, the newly evolved, eco-friendly, room-temperature ionic liquids (RTILs) gained much popularity as substitutes for the toxic organic solvents.[20–23] In the regular organic synthesis, appearance of numerous reports of reactions using RTILs further demonstrates the influence of the ionic liquids as a reaction medium. Similar experiments with respect to the supramolecular synthesis, however, are scarce, except for a few reports that appeared in the recent literature.[24–27]



Results and Discussion

In our exploration to utilize this new class of solvent media, RTILs, we focused our attention on evaluating whether such conditions would yield identical products/assemblies to those observed at ambient conditions. For this purpose, we have chosen the synthesis of Cu(II) and Ni(II) assemblies with 4,4′-bipyridine and 2,2′-bipyridine, respectively, using 1-ethyl-3-

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methyl-imidazolium tetrafluoroborate, an ionic liquid, as a crystallization solvent. We describe the exotic architectures evolved from the RTIL medium, that are distinctly different from those obtained by conventional methods.[28–30]

A mixture of 12.1 mg $Cu(NO_3)_2.3H_2O$ and 7.8 mg 4,4′-bipyridine (*bpy*) in 0.2 mL 1-ethyl-3-methlyimidazolium tetrafluoroborate was placed in a pyrex glass tube (6 cm length) and sealed under vacuum. The tube was heated for 48 hrs at 130 °C and subsequently cooled to room temperature. Single crystals, thus, obtained were isolated and dried under vacuum.

The structure determination[31] by single crystal X-ray diffraction method reveals that the asymmetric unit is a cationic coordination polymer $[Cu(bpy)_2]^+NO_3^-$, suggesting reduction of $Cu(II) \rightarrow Cu(I)$, and with each Cu(I) coordinating to four molecules of *bpy*, [33] which are arranged in a tetrahedral manner. The Cu(I) binds to *bpy* molecules through Cu–N dative bonds with an average distance of 2.047 Å. The coordination sphere is shown in Figure 1. The product obtained from a hydrotherma reaction was found to be a trigonal complex.[28]

In addition, the three-dimensional packing of the molecules is interesting when the adjacent tetrahedrons are held together yielding a diamondoid network. A representative diamondoid is shown in Figure 2a.

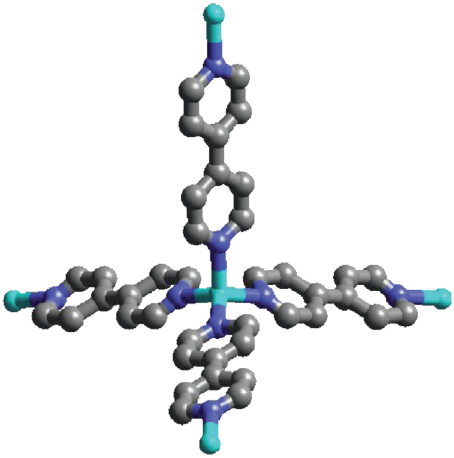

Figure 1.
Coordination of Cu(I) with 4,4′-bipyrdine (*bpy*) forming a tetrahedral geometry.

Because of the large dimension of *bpy* molecules (~11 Å), each diamondoid network possesses a huge void space, which is effectively filled by the catenation of three such adjacent networks as shown in Figure 2b. These interpenetrated diamondoid networks ultimately form channels of dimension (~12 Å) along the *c*-axis, which is occupied by nitrate anions (Figure 3). Cu(I) is known to form such diamondoid networks, however, they are limited in

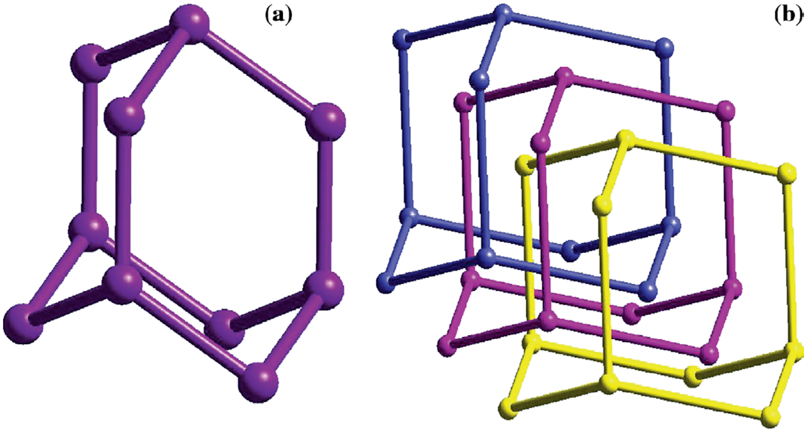

Figure 2.
(a) Diamondoid network formed between Cu(I) (spheres) and *bpy* molecules (cylinders). (b) Interpenetration of the adjacent diamondoid networks in a 3-fold manner.

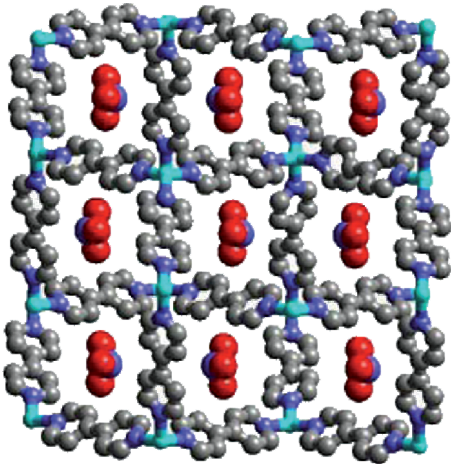

Figure 3.
Channels formed in the coordination complex, $[Cu(bpy)_4]^+(NO_3)^-$ along the *c*-axis. The nitrate anions are shown in ball mode. Only one of the orientations of *bpy* molecules is shown.

number. Furthermore, the present complex differs from other structures in the process of catenation/interpenetration, since in our study, there is only a 3-fold (Figure 2b) but not a 4-fold catenation as observed in the related structures prepared by other procedures.[28] We believe that such a difference is due to the function of the ionic liquids as a reaction medium and further signifies their utilization in the supramolecular synthesis.

Similarly, a reaction carried out between $Ni(NO_3)_2 \cdot 6H_2O$ and 2,2′-bipyrdine (*bpy*′) yields a complex, $[Ni(bpy')_2NO_3]^+(NO_3)^-$ from IL. However, a different complex, $[Ni(bpy')(NO_3)(H_2O)_3]^+(NO_3)^-$ was reported by conventional synthetic procedures.[30] The crystal structure determination[31] of $[Ni(bpy')_2NO_3]^+(NO_3)^-$ reveals that each Ni(II) is coordinated to two *bpy*′ molecules through Ni–N dative bonds with an average distance of 2.033 Å. Ni(II) completes its hexacoordination through binding to a nitrate anion forming Ni–O bonds in a chelated mode, with an average distance of 2.125 Å. An ORTEP drawing of the coordination geometry and the asymmetric unit are shown in Figure 4a.

In three-dimensional arrangement, the complex packs in a rather simple pattern forming staked zig-zag networks. The packing is shown in Figure 5. In each typical sheet (Figure 5b), the adjacent coordination spheres are held together through C–H···O hydrogen bonds formed between the H-atoms on *bpy*′ and O-atoms on nitrate anion, illustrating the influence of hydrogen bonds even in the coordination polymers. Thus, $[Ni(bpy')_2(NO_3)]^+(NO_3)^-$ do not form extended coordination polymer network that was observed in the complex $[Cu(bpy)_2]^+NO_3^-$ as described above.

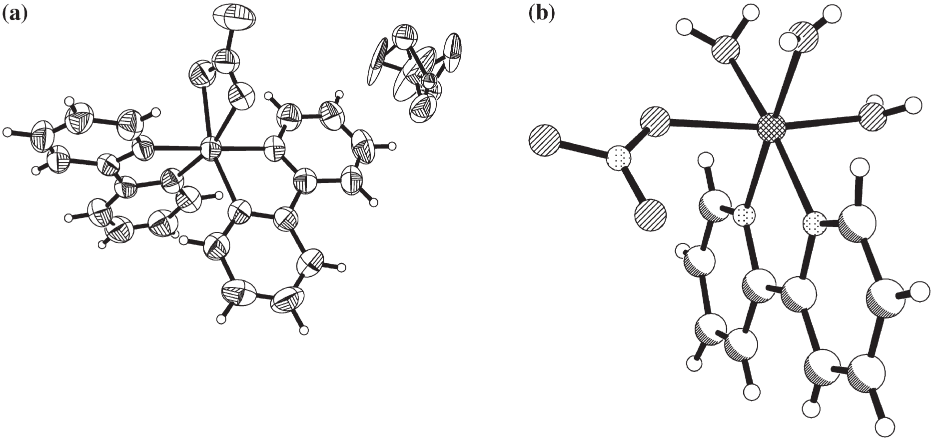

Figure 4.
a) ORTEP drawing of the complex formed between Ni(II) and *bpy*′ from the IL. b) Coordination of Ni(II), which is different from that shown in (a), when the complex was prepared from conventional methods.

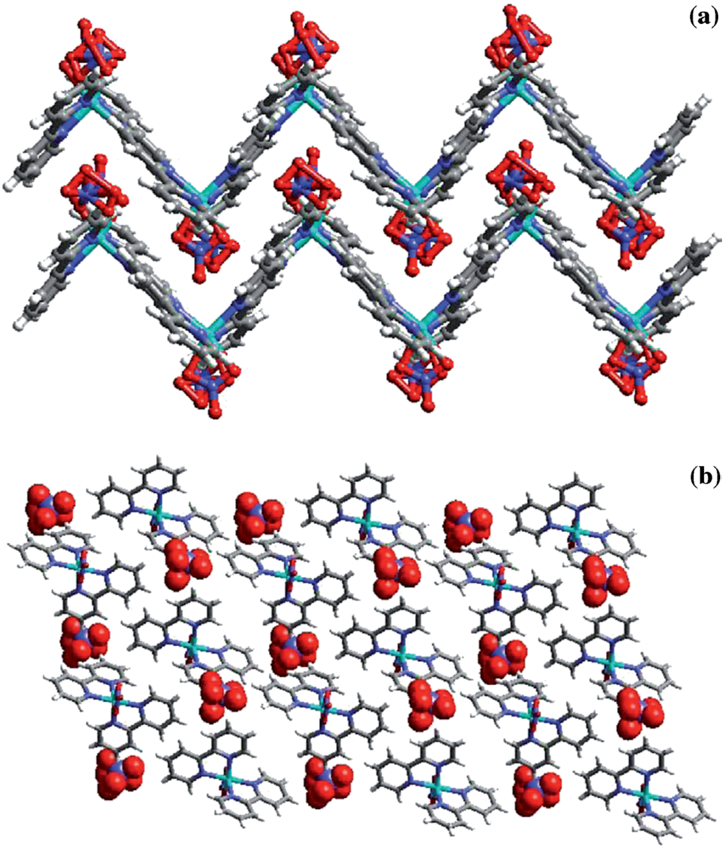

Figure 5.

a) Stacking of crinkled sheets of coordination moieties and nitrate anions in the three-dimensional arrangement of the crystal lattice b) Arrangement of discrete coordination units within a typical sheet. Each unit is connected to the neighbours through C–H···O hydrogen bonds formed by nitrate anions, which are shown in ball mode.

Conclusion

In conclusion, two novel coordination complexes, $[Cu(\textit{bpy})_2]^+(NO_3)^-$ and $[Ni(\textit{bpy}')_2(NO_3)]^+(NO_3)^-$ that were, exclusively, obtained by performing the reaction in an ionic liquid have been reported. The study vividly illustrates that RTILs could be used as alternative for the organic solvents in the supramolecular synthesis too. Furthermore, formation of diverse types of products without the involvement of the crystalline lattice, instead of the path followed by the conventional procedures suggests that RTILs could serve as potential candidates for the polymorphism studies. In continuation of the observation reported herein, several experiments are presently in progress in our laboratory to explore further the effectiveness of RTILs in the formation of unusual products, polymorphs, etc.

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[31] *Crystal data* of $\mathbf{[Cu(bpy)_2]^+\ NO_3^-}$: $M = 421.79$, monoclinic, $C2/m$, $a = 17.470(4)$, $b = 16.437(4)$, $c = 7.155(2)$ Å, $\beta = 99.00^\circ$ (4), $V = 2029.3(9)$ Å^3, $Z = 4$, $\rho_{calc} = 1.381$ g cm^{-3}, $T = 298$ K, μ(Mo-K$_\alpha$) = 1.105 mm^{-1}, 8078 reflections measured, $R_1 = 0.101$, $wR_2 = 0.273$. *Crystal data* of $[\mathbf{Ni}(\boldsymbol{bpy'})_2(\mathbf{NO_3})]^+(\mathbf{NO_3})^-$: $M = 495.10$, monoclinic, $P2_1/n$, $a = 10.528(2)$, $b = 12.949(2)$, $c = 16.210(3)$ Å, $\beta = 106.19^\circ$ (9), $V = 2122.2(1)$ Å^3, $Z = 4$, $\rho_{calc} = 1.550$ g cm^{-3}, $T = 298$ K, μ(Mo-K$_\alpha$) = 0.966 mm^{-1}, 12844 reflections measured, $R_1 = 0.078$, $wR_2 = 0.212$.

[32] It is quite interesting to note that all the four *bpy* molecules and also the nitrate anion are disordered.

[33] A mixture of $Ni(NO_3) \cdot 6H_2O$ (14.5 mg, 0.05 mmol) and 2,2′-bipyridine (9.11 mg, 0.05 mmol) was added to 0.2 mL of 1-ethyl-3-methylimidazolium tetrafluoroborate in a pyrex glass tube. It was then sealed under vacuum and heated at 130 °C for 48 hours and subsequently cooled down to room temperature. Pale red block crystals, thus obtained, were isolated and dried under vacuum.