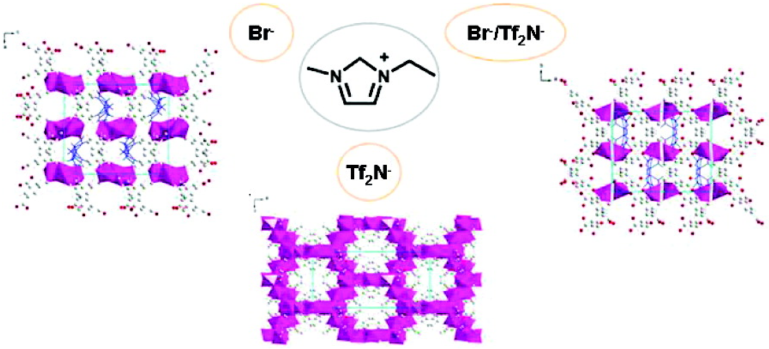
Communication

Anion Control in the Ionothermal Synthesis of Coordination Polymers

Zhuojia Lin, David S. Wragg, John E. Warren, and Russell E. Morris

J. Am. Chem. Soc., **2007**, 129 (34), 10334-10335• DOI: 10.1021/ja0737671 • Publication Date (Web): 04 August 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Anion Control in the Ionothermal Synthesis of Coordination Polymers

Zhuojia Lin, David S. Wragg, John E. Warren, and Russell E. Morris*

School of Chemistry, University of St. Andrews, St Andrews, Fife, Scotland, U.K. KY16 9ST

Received May 25, 2007; E-mail: rem1@st-and.ac.uk

The most common method of controlling the structure of a product in a solvothermal synthesis uses structure directing agents (SDAs, sometimes also called templates). In the synthesis of porous materials such as zeolites and some types of coordination polymers these are often organic cations of varying sizes, which are incorporated into the structure of the product. Templating is much less common in the preparation of coordination polymer materials but can still produce interesting solids. In this Communication we report an alternative method of controlling the structure of a product in a solvothermal reaction of coordination polymers. In this method we use the anions present in ionic liquids to control the structure of materials formed in ionothermal synthesis. The cations of the ionic liquid, which in this study are always the same, are incorporated into the resultant materials, but the anions are not. Of particular interest is that mixed anion ionic liquids show different product selectivity to single anion liquids, indicating the level of structure direction available in this synthetic methodology.

Ionothermal synthesis has been used recently to produce zeotypes,[1,2] supramolecular architectures,[3] and coordination polymers/metal organic frameworks (MOFs).[4,5] To date, much of the work on ionothermal synthesis has concentrated on the use of 1-ethyl-3-methyl imidazolium bromide (EMIm-Br) as the solvent. Ionic liquids have been referred to as “designer solvents” as their properties, including melting point, density, viscosity, and miscibility with water, can be easily altered by judicious choice of cations and anions.[6] The influence of the anion deserves particular attention; for example, replacing the Br^- in EMIm-Br with bis((trifluoromethyl)sulfonyl)amide (Tf_2N^-) dramatically decreases the melting point (from 81 to −3 °C) and the water solubility (from highly water-soluble to 1.4 wt % water content saturated at 20 °C).[7] EMIm-Tf_2N displays exceptional properties, combining high hydrophobicity, low polarity, good thermal stability, low viscosity, and a very low melting point and has been used in synthetic and electrochemical applications.[7b] Nevertheless, very few investigations have been carried out on how the choice of anion in ILs affects the reaction outcome in materials synthesis, although our recent illustration of chiral induction by a chiral IL anion is one example.[5]

Here we report four cobalt compounds $(EMIm)_2[Co_3(TMA)_2(OAc)_2]$ **1**, $(EMIm)[Co(TMA)]$ **2**, $[Co_5(OH)_2(OAc)_8](H_2O)_x$ **3**, and $(EMIm)[Co_2(TMA)_4H_7(22bpy)_2]$ **4** (TMA = trimesate and 22bpy = 2, 2′-bipyridine).[8,9] The controlling feature of the synthesis is the IL anion chosen. Compound **1** is formed using EMIm-Br as the solvent, **3** and **4** when EMIm-Tf_2N is the solvent, and **2** when a mixture of EMIm-Br and EMIm-Tf_2N (1:1 molar ratio) is used.

Compound **1** was synthesized from EMIm-Br in a sealed autoclave and is isostructural to the nickel analogue $(EMIm)_2[Ni_3(TMA)_2(OAc)_2]$.[4a] The liquid solubilizes all the starting materials very well, and the mechanism of formation appears be solution mediated. The whole network can be described as a (3,6)-connected net constructed by octahedral $Co_3(\mu^2\text{-}\eta^1{:}\eta^2\text{-}CH_3COO)_2(\mu^2\text{-}RCOO)_4(\textit{chelating}\text{-}RCOO)_2$ secondary building units (SBUs) and topologically 3-connected TMA ligands.

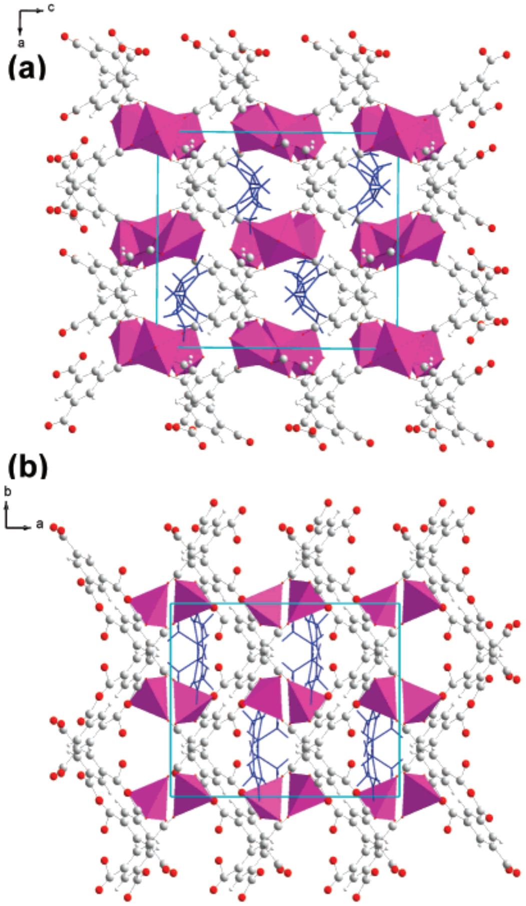


Figure 1. The structures of **1** (a) synthesized from EMIm-Br and $Co_2(COO)_6$ SBU and **2** (b) synthesized using mixed EMIm-Br/EMIm-Tf_2N: Co, purple octahedra (**1**) or tetrahedra (**2**); C, gray; O, red; H, white. The $EMIm^+$ cations in **1** are severely disordered. $EMIm^+$ (blue line) outside the unit cells are omitted for clarity.

When the reaction was carried out in a less polar, more hydrophobic solvent, that is, using an EMIm-Br/EMIm-Tf_2N (1:1 molar ratio) mixture a different 3D anionic framework **2** was formed. The overall structure is built from dinuclear $Co_2(\textit{syn,anti}\text{-}COO)_2(\textit{mono}\text{-}COO)_4$ secondary building units (SBUs) where each cobalt is tetrahedrally coordinated (Figure 1). Four SBUs are arranged in rectangular grids with dimensions of ~5 Å × 11 Å, and which are further arranged in a herringbone packing mode in the *ab* plane to form an infinite layer. Different layers are connected into a 3D network through stacking in an ABAB sequence. The staggered layers result in rectangular void space with small windows of ~4 Å × 4 Å along the *c*-axis. Each rectangular void encapsulates two $EMIm^+$ ions to compensate the negative-charge of the framework.

The solvent polarity has great influence on the coordination behaviors of the metal atoms, and the partial replacement of EMIm-

10.1021/ja0737671 CCC: $37.00 © 2007 American Chemical Society

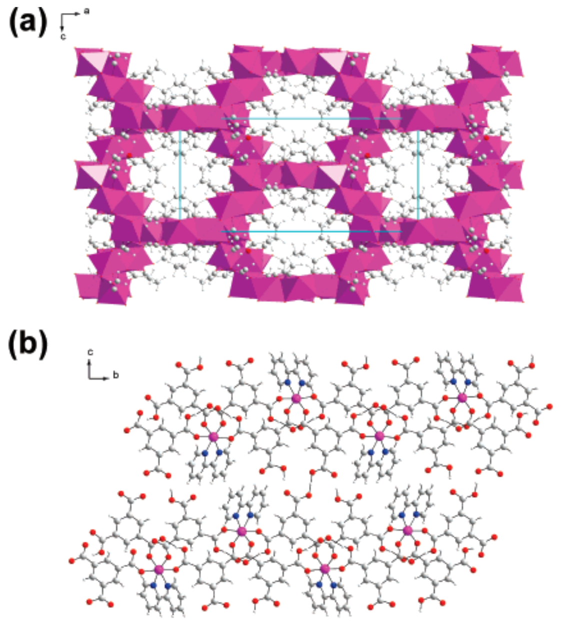


Figure 2. Inorganic framework of **3** (a) and supramolecular framework of **4** (b) from EMIm-Tf_2N: Co, purple ball or polyhedron; C, gray; N, blue; H, white. $(EMIm)^+$ in **4** are omitted.

Br with EMIm-Tf_2N leads to the change of coordination geometries of cobalt from octahedral in **1** to tetrahedral in **2**. Further reducing the solvent polarity results in poor solubilization of the starting materials, and only a mixture of trimesic acid and an inorganic compound $[Co_5(OH)_2(OAc)_8](H_2O)_x$ **3** was obtained from EMIm-Tf_2N. In the structure of **3**, three crystallographically distinct cobalt atoms in octahedral geometry are linked by one μ^3-OH and four different acetates (one η^1:η^1, two η^1:η^2 and one η^2:η^2) into a 3D condensed hydroxide network with a nearly hexagonal motif when viewed along the *b*-axis (Figure 2). Compound **3** can be prepared by solvothermal treatment of cobalt(III) acetylacetonate in a THF solution containing 4 vol % H_2O.[11] This accords with the solvatochromatic studies that ILs have polarities similar to those of short-chain alcohol and other polar solvents.[7a]

To help solubilize the starting materials in the EMIm-Tf_2N ionic liquid, 2,2′-bipyridine was added as a co-ligand, yielding (EMIm)-$[Co_2(TMA)_4H_7(22bpy)_2]$, **4**, as the major product. Compound **4** has a 2D layer structure connected by very strong hydrogen bonding into a 3D supramolecular framework. While in **1** and **2** the TMA units bind in several different modes to the cobalt, the TMAs in **4** connect two cobalt atoms only via monodentate linkages. As two of the coordination sites are blocked by 2,2′-bipyridine, the metal centers are linked in a seesaw shape into an infinite fluctuated (4,4)-square net. Four carboxylate groups around the metal center form two very short $R_1^1(8)$ hydrogen bonds (O⋯H⋯O = 2.435(5) and 2.489(5) Å), which helps cobalt to retain the octahedral coordination geometry. Adjacent layers are held together by hydrogen bonds among the uncoordinated carboxylate groups (O⋯H⋯O = 2.429(8) and 2.651(5) Å). The $EMIm^+$ cations are highly disordered and situated between layers.

A well-known function of the anion is to control the amount of water present in the IL. EMIm-Br is hygroscopic and contains a significant amount of water even after a moderate drying process.[11] Although this may be a problem for some applications, the trace of water can act as a mineralizer and is essential for the crystallization of the coordination polymers in these reactions.

In summary we synthesized two anionic 3D coordination frameworks and one 2D layer compound from three relevant ionic liquids with various solvent polarity/hydrophibicity, controlled by changing the anion in the IL. Hydrophilic ionic liquids containing small amounts of water tend to facilitate the production of framework compounds, while the hydrophobic nature of the EMIm-Tf_2N solvent results in poor solubilization of metal ions and organic ligands, which in turn inhibits the formation of polymeric structures. We have also shown that adding a solubilizing agent such as 2,2′-bipyridine, can be used to circumvent some of the problems associated with the use of hydrophobic ionic liquids.

Acknowledgment. We thank the EPSRC (U.K.) for funding.

Supporting Information Available: Crystallographic information (CIF) for **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. *Nature* **2004**, *430*, 1012. (b) Parnham, E. R.; Morris, R. E. *Acc. Chem. Res.*, published online, June 21, 2007, http://dx.doi.org/10.1021/ar700025k.

(2) (a) Parnham, E. R.; Wheatley, P. S.; Morris, R. E. *Chem. Commun.* **2006**, 380. (b) Parnham, E. R.; Morris, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 2204. (c) Wang, L.; Xu, Y.; Wei, Y.; Duan, J.; Chen, A.; Wang, B.; Ma, H.; Tian, Z.; Lin, L. *J. Am. Chem. Soc.* **2006**, *128*, 7432.

(3) Reichert W. M.; Holbrey, J. D.; Vigour K. B.; Morgan T. D.; Broker G. A.; Rogers, R. D. *Chem. Commun.* **2006**, 4767.

(4) (a) Lin, Z.; Wragg, D. S.; Morris, R. E. *Chem. Commun.* **2006**, 2021. (b) Dybtsev, D. N.; Chun H.; Kim K. *Chem. Commun.* **2004**, 1594. (c) Jin, K.; Huang, X.; Pang, L.; Li, J.; Appel, A.; Wherland, S. *Chem. Commun.* **2002**, 2872.

(5) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880.

(6) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(7) (a) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinhein, Germany, 2003. (b) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168.

(8) Synthesis: for **1** $Co(OAc)_2{\cdot}4H_2O$ (380 mg, 1.5 mmol, Fisons), Trimesic acid (TMA-H_3, 210 mg, 1 mmol, Avocado) and ~10 mmol EMIm-Br were sealed and heated in a 23 mL Teflon-lined stainless steel autoclave at 150 °C for 3 days. Dark-purple block crystals of **1** were collected with 75% yield. The similar method was followed for other compounds. For **2** $Co(OAc)_2{\cdot}4H_2O$ (1.5 mmol), TMA-H_3 (1 mmol) and ~5 mmol EMIm-Br and ~5 mmol EMIm-Tf_2N were mixed and heated at 150 °C for 3 days. Purple plate crystals were collected with 65% yield. Some samples of **2** contain a small amount of Li^+ impurity that is present in the EMIM-Tf_2N starting material. For **3** $Co(OAc)_2{\cdot}4H_2O$ (1.5 mmol), TMA-H_3 (1 mmol) and ~10 mmol EMIm-Tf_2N were mixed and heated at 110 °C for 5 days. A mixture of orange bar crystals and white solid was collected with a total 50% yield. For **4** $Co(OAc)_2{\cdot}4H_2O$ (1.5 mmol), TMA-H_3 (1 mmol), 22bpy (2 mmol) and ~10 mmol EMIm-Tf_2N were mixed and heated at 150 °C for 3 days. Orange plate crystals were collected with total 60% yield.

(9) Crystal data for **1**: $T = 90(2)$ K, $\lambda = 0.67130$ Å, orthorhombic, *Pbca*, $a = 14.2616(4)$ Å, $b = 16.1525(5)$ Å, $c = 16.4867(5)$ Å, $V = 3797.9(2)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.629$ Mg/m^3, $\mu = 1.373$ mm^{-1}, $2\theta = 2.98$ to 26.99°, data/restraints/parameters = 4883/0/251, GOF = 1.098, $R_1 = 0.0454$, wR_2(all) = 0.1328. Crystal data for **2**: $T = 113(2)$ K, $\lambda = 0.71073$ Å, orthorhombic, *Pbca*, $a = 15.425(2)$ Å, $b = 12.184(2)$ Å, $c = 16.059(2)$ Å, $V = 3018.1(7)$ Å^3, $Z = 8$, $D_c = 1.558$ Mg/m^3, $\mu = 0.800$ mm^{-1}, $2\theta = 2.48$ to 26.00°, data/restraints/parameters = 2828/0/235, GOF = 1.198, $R_1 = 0.0882$, wR_2(all) = 0.2199. Crystal data for **3**: $T = 113(2)$ K, $\lambda = 0.71073$ Å, tetragonal, *I*4(1)/*a*, $a = 23.705(3)$ Å, $c = 11.409(2)$ Å, $V = 6410.6(18)$ Å^3, $Z = 8$, $D_c = 1.726$ Mg/m^3, $\mu = 2.608$ mm^{-1}, $2\theta = 1.98$ to 25.99°, data/restraints/parameters = 3118/0/196, GOF = 1.187, $R_1 = 0.0906$, wR_2(all) = 0.2262. Crystal data for **4**: $T = 113(2)$ K, $\lambda = 0.71073$ Å, monoclinic, *P*2(1)/*c*, $a = 6.579(1)$ Å, $b = 16.775(3)$ Å, $c = 11.409(2)$ Å, $\beta = 93.944(4)$°, $V = 3002.0(8)$ Å^3, $Z = 2$, $D_c = 1.400$ Mg/m^3, $\mu = 0.636$ mm^{-1}, $2\theta = 1.93$ to 26.00°, data/restraints/parameters = 5684/0/391, GOF = 1.065, $R_1 = 0.0767$, wR_2(all) = 0.2014. The program SQUEEZE was used to model the electron density in the pores from the severely disordered $EMIm^+$ cations in **1** and **4.**

(10) Kuhlman, R.; Schimek, G. L.; Kolis, J. W. *Inorg. Chem.* **1999**, *38*, 194.

(11) (a) Cammarata, L.; Kazarian, S. G.; Slater, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.

JA0737671