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Ionothermal Synthesis of Polyoxometalates

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Owing to the potential applications of transition-metal-oxide clusters or polyoxometalates (POMs) in catalysis, gas storage, separation, materials science, nanotechnology, chemical sensing, environmental decontamination, and medicine, their design and synthesis have attracted considerable attention in functional solid-state materials.[1,2] They provide an unmatched variety of structural motifs with different topologies and sizes that are potential building blocks for the development of extended solids. The chemistry of POMs is under rapid development and these materials include a range of high-dimensional, porous, and tangled structures, multifunctional nanomaterials, protein-sized molecules, and porous capsule materials, as well as single-molecule magnets and electrochromic materials.[3]

Conventional solution synthesis and hydro- or solvothermal synthesis are two main methods for the synthesis of POMs. In conventional synthesis under standard conditions, the operations are easy to conduct and most of the reactions have good reproducibility. However, the use of water or organic solvents (e.g. acetonitrile, methanol, and pyridine) limits the reaction temperature. Thus, hydro- or solvothermal processes have been applied for the preparation of POMs.[4] Under these conditions, metastable or intermediate phases can be synthesized easily leading to the kinetic phases that are most likely to be isolated. The reduced viscosity and the increased ionicity of the solvents enhance the diffusion of the reactants and improve their solubility. However, traditional solvothermal methods are based on the generation of significant autogenous pressure when the reaction mixture is heated in a sealed container. Solvothermal synthesis has also some intrinsic shortcomings: the general reproducibility of the reactions requires perfect control of reaction parameters, low solubility of the precursors, and still limited reaction temperature because of safety concerns.[5,6]

As a consequence of the growing interest in the applications and various challenges associated with the traditional synthesis methods, researchers have focused on developing new synthetic approaches. Morris and co-workers introduced ionothermal synthesis—a relatively new and more effective method for the synthesis of crystalline solids that uses ionic liquids (ILs) instead of water or organic solvents.[5] Wang et al., Pakhomova et al., and others have extended this approach for the synthesis of POMs because ILs have little or no volatility, which means even at elevated temperatures they produce no autogenous pressure; thus POMs can be prepared at elevated temperature yet ambient pressure.[6] As ILs are simply composed of ions, the enthalpy of vaporization is significantly higher than that of water or organic solvents. This property is the key motivation to consider ILs as green alternatives to volatile organic solvents.[5]

ILs have numerous additional properties, such as high chemical and thermal stability, a wide liquid range, and low toxicity, which make them ideal solvents for organic and inorganic synthesis.[7] Owing to their ionic character, they are polar solvents suitable for the dissolution of many different types of inorganic precursors, even though this depends significantly on the composition of the ILs chosen. Many ILs, particularly those derived from imidazolium and quaternary ammonium salts, are chemically almost comparable to the organic cations that are commonly used as structure-directing agents or templates in the preparation of coordination polymers by the hydrothermal method.

Replacing the solvent and the organic template with a single IL is the basis of the ionothermal method. In ionothermal synthesis, an IL acts as a solvent, potential template, or structure-directing species for the preparation of solid materials.[5] Changing the anionic component of the IL can result in the selective synthesis of different POMs. The ionothermal method facilitated the synthesis of new POMs, for example, a high-nuclearity transition-metal-substituted polyoxometalate with an unprecedented polyoxoanion, composed of three $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ Keggin moieties connected by a $\{\text{WFe}_9\}$ cluster core (Figure 1),[6a] and a one-dimensional supramolecular chain-like structure constructed from $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anions.[6b] Moreover, an excellent quantum spin liquid candidate, $[\text{NH}_4]_2[\text{C}_7\text{H}_{14}\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$, which contains a frustrated magnetic $S={}^{1}/_{2}$ Kagomé network of d^1 V^{4+} ions,[5b] and, for the first time, two- and three-dimensional polyoxometalate-based metal–organic frameworks (PMOFs) have also been prepared by this method.[6b]

Ionothermal synthesis has numerous additional advantages:

- The weak coordinating ability of ILs can facilitate the self-assembly of the polyoxoanions.

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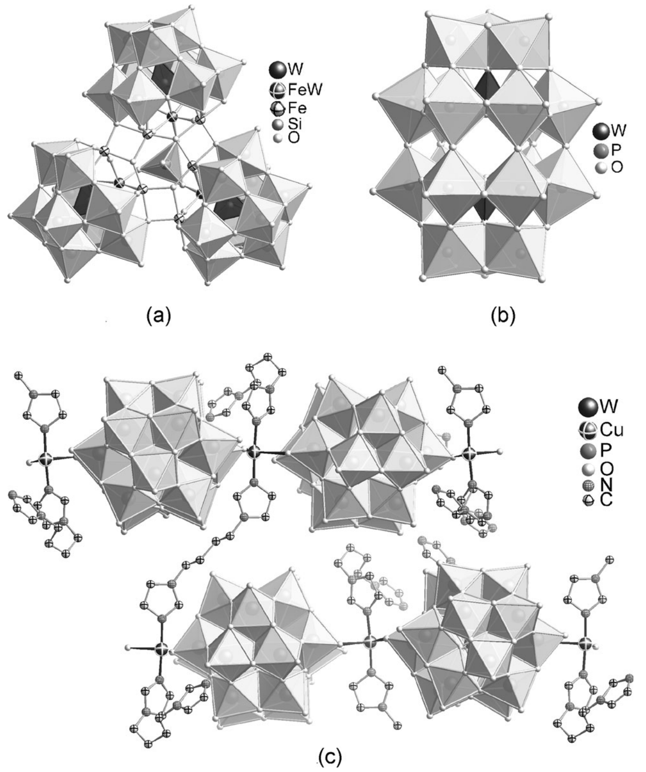

Figure 1. Structures of various heteropolyoxometalates synthesized by ionothermal method: a) An unprecedented polyoxoanion, composed of three $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ Keggin moieties connected by a {WFe_9} cluster core in $[\text{Emim}]_8\text{Na}_9[\text{WFe}_9(\mu_3\text{-O})_3(\mu_2\text{-OH})_6\text{O}_4\text{H}_2\text{O}(\text{SiW}_9\text{O}_{34})_3]\cdot 7\,\text{H}_2\text{O}$ (Emim = 1-ethyl-3-methylimidazolium)); b) $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anion, which forms a supramolecular chain in $\text{H}_3(\text{Tea})(\text{Bmim})_3[\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 3\,\text{H}_2\text{O}$ (Tea = triethylamine, Bmim = 1-methyl-3-ethylimidazole); c) a layer of interconnected clusters in $\text{Cu}^{\text{II}}(\text{Bbi})_{1.5}(\text{H}_2\text{Bbi})_2[\text{P}_2\text{W}_{18}\text{O}_{62}]$ (Bbi = 1,1-(1,4-butanediyl)-bis(imidazole)).

- The higher solubility of inorganic precursors in ILs can significantly improve their reactivity in the reaction mixture over that observed in traditional hydro- or solvothermal synthesis.
- In contrast to hydro- or solvothermal synthesis, almost no competing reactions are observed between solvents and frameworks in ionothermal synthesis, which reduces the complexity of the whole reaction system. In addition, the activity of the trace water molecules in the ILs is minimal.
- The presence of the trace hydrated halide ions in ILs may support the growth of the open frameworks.
- Controllable parameters such as ILs' acidity can be adjusted to satisfy the pH conditions required for the synthesis of different types of POMs.
- New functional materials can be fabricated if the cationic parts of ILs are combined with the polyoxoanions, and these materials may find potential applications as biocatalysts, electrocatalysts, or solid lubricants.[6c,8]

This emerging approach not only demonstrates the advantages of using ILs as solvents in the preparation of new kinds of POMs and PMOFs, but also facilitates more efficient synthesis. The most important feature of ionothermal synthesis is that it is not limited to porous solids, POMs, and PMOFs but is potentially applicable to any material that can be prepared using solution-state "soft-chemical" approaches. ILs are often regarded as "designer solvents" and new ILs, for example based on the Bbi cation,[6b] could be further developed to prepare PMOFs with novel topologies and interesting properties. Likewise, ILs can also be used to control the redox chemistry of metals. They can stabilize a particular oxidation state or a combination of oxidation states that are otherwise difficult to access. Especially high oxidation states will promote the formation of multidimensional frameworks. Besides the application in synthesis, ILs may also serve in the screening of electroactive systems.

The future of ionothermal synthesis is exciting, and a better understanding of the principles that underpin the assembly mechanisms of POMs should lead to their designed construction. Therefore, this modern synthetic route may be a bridge joining structural design with the emerging class of composite and nanomaterials. Thus, ILs are also anticipated to play an important role in the synthesis of POM-based integrated nanosystems.[9]

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[1] a) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; b) H. N. Miras, G. J. T. Cooper, D.-L. Long, H. Bögge, A. Müller, C. Streb, L. Cronin, *Science* **2010**, *327*, 72–74; c) T. Liu, M. L. K. Langston, D. Li, J. M. Pigga, C. Pichon, A. M. Todea, A. Müller, *Science* **2011**, *331*, 1590–1592.

[2] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; b) A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.* **2010**, *110*, 6009–6048.

[3] a) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780–1803; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758; b) M. Ishaque Khan, *J. Solid State Chem.* **2000**, *152*, 105–112.

[4] a) Z. Shi, S. Feng, L. Zhang, G. Yang, J. Hua, *Chem. Mater.* **2000**, *12*, 2930–2935; b) J.-W. Zhao, J. Zhang, S.-T. Zheng, G.-Y. Yang, *Inorg. Chem.* **2007**, *46*, 10944–10946.

[5] a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012–1016; b) F. H. Aidoudi, D. W. Aldous, R. J. Goff, A. M. Z. Slawin, J. P. Attfield, R. E. Morris, P. Lightfoot, *Nature Chem.* **2011**, *3*, 801–806.

[6] a) S. Lin, W. Liu, Y. Li, Q. Wu, E. Wang, Z. Zhang, *Dalton Trans.* **2010**, *39*, 1740–1744; b) H. Fu, Y. Li, Y. Lu, W. Chen, Q. Wu, J. Meng, X. Wang, Z. Zhang, E. Wang, *Cryst. Growth Des.* **2011**, *11*, 458–465; c) W. L. Chen, B. W. Chen, H. Q. Tan, Y. G. Li, Y. H. Wang, E. Wang, *J. Solid State Chem.* **2010**, *183*, 310–321; d) A. S. Pakhomova, S. V. Krivovichev, *Inorg. Chem. Commun.* **2010**, *13*, 1463–1465.

[7] a) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2007**; b) E. Ahmed, M. Ruck, *Dalton Trans.* **2011**, *40*, 9347–9357; c) E. Ahmed, M. Ruck, *Coord. Chem. Rev.* **2011**, *255*, 2892–2903.

[8] Z. Li, Q. Zhang, H. Liu, P. He, X. Xu, J. Li, *J. Power Sources* **2006**, *158*, 103–109.

[9] D.-L. Long, L. Cronin, *Chem. Eur. J.* **2006**, *12*, 3698–3706.