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Reactions of metal salts with bronsted acidic ionic liquid: Formations of imidazole template metal sulfates or imidazole-metal complexes

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ABSTRACT

The reactions of metal salts with Bronsted acidic ionic liquid [HMIM][HSO_4] in ethanol were investigated. Zr($OPr)_4$, $ZnCl_2$ or $MnCl_2$ reacted with [HMIM][HSO_4] via an anion exchange and resulted in the formation of imidazole template sulfates $[HMIM]_2Zr[SO_4]_3[DMSO]_2$ (**1**), $[HMIM]_2Zn[SO_4]_2$ (**2**) and $[HMIM]_2Mn[SO_4]_2$ (**3**), respectively. On the other hand, $Cu(OAc)_2$ interacted with imidazole to form an imidazole-Cu complex $[MIM]_4Cu[HSO_4]_2$ (**4**). The imidazole template sulfates present various crystal structures, in which $[HMIM]_2Zr[SO_4]_3[DMSO]_2$ (**1**) has zero dimensional monomeric structure made up of $[Zr(SO_4)_3(DMSO)_2]^{2-}$ anions and $[HMIM]^+$ cations. While, $[HMIM]_2Zn[SO_4]_2$ (**2**) and $[HMIM]_2Mn[SO_4]_2$ (**3**) exhibit one dimensional metal–organic framework which consist of infinite linear chains linked by SO_4 units. Compound **4** is an imidazole-metal complex, in which four imidazoles coordinate to Cu(II) to form tetragonal structure compensating the charges with protonated sulfates. Additionally, the magnetic property of compound **3** is investigated to find that it presents a weak antiferromagnetic property probably due to the coupling interactions between the neighboring Mn(II) centers.

1. Introduction

Ionic liquids are attracting considerable attention owing to their unique physicochemical properties: extremely low volatility, wide liquid temperature range, good thermal stability, good dissolving ability, excellent microwave absorbing ability, designable structure, high ionic conductivity, wide electrochemical window, etc [1–7]. They may be seen as a tool with potential applications in sustainable processes such as solvent replacement and in catalytic reactions, electrochemical devices, and the synthesis of nanoparticles. Seldom researches consider about the interaction between ionic liquids and other chemicals. In our previous research, we have proved the anion exchange reactions of $[BF_4]^-$ or $[PF_6]^-$ based ionic liquids with titanium or zirconium alcoholate to form $[Ti(OH)_6]^{2-}$ or $[Zr(OH)_6]^{2-}$ imidazolium or pyridium complexes by using ethanol as solvent [8]. In contrast, other anions of ionic liquids such as Cl^-, Br^-, OTs^- or NTf_2^- lead to the formation of the $Ti_7O_4(OEt)_{20}$ cluster via the control hydrolysis of $Ti(O^iPr)_4$ [9]. In this work, we investigated the hydrolysis reactions of $Ti(O^iPr)_4$ or $Zr(OPr)_4$ in Bronsted acidic ionic liquid [HMIM][HSO_4] using ethanol as solvent as well. The reaction of $Ti(O^iPr)_4$ gave rise to an unknown white solid, however, the reaction of $Zr(OPr)_4$ led to the formation of imidazole template sulfate $[HMIM]_2Zr[SO_4]_3[DMSO]_2$ (**1**) via the anion exchange reaction. Furthermore, we extended this method to synthesize other imidazole template sulfates. $[HMIM]_2Zn[SO_4]_2$ (**2**), $[HMIM]_2Mn[SO_4]_2$ (**3**) and $[MIM]_4Cu[HSO_4]_2$ (**4**) were achieved successfully.

2. Results and discussion

2.1. Synthesis

$Ti(O^iPr)_4$ or $Zr(OPr)_4$ was added to the ethanol solution of [HMIM][HSO_4]. The temperature was raised up to reflux accompanying with precipitation of white solids. This phenomenon was different to the reaction of $Ti(O^iPr)_4$ or $Zr(OPr)_4$ in other ionic liquids, where a clear solution were obtained normally. After reacted for 4 h, the white solids were collected. The solids of the reaction of $Ti(O^iPr)_4$ were analyzed with FTIR spectra to find that there were obvious absorptions assigned to imidazolium. We tried to recrystalize it, however, it cannot be dissolved in any organic solvent or water. The product was not further identified. In comparison, the product of $Zr(OPr)_4$ can be dissolved in a mixed solvent of EtOAc/acetonitrile/DMSO. Cubic-like colorless single crystals were obtained, which were identified as $[HMIM]_2Zr[SO_4]_3[DMSO]_2$ (**1**)

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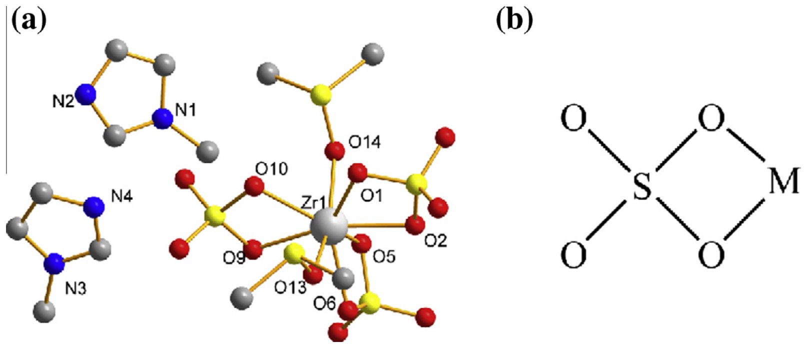
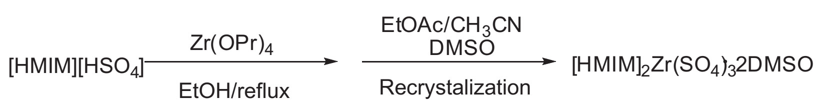


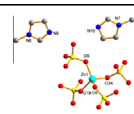
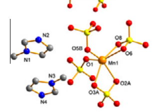
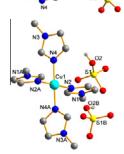
Fig. 1. (a) Ball-and-stick representation of $[HMIM]_2Zr[SO_4]_3[DMSO]_2$. $[Zr(SO_4)_3(DMSO)_2]^{2-}$ is coordinated through hydrogen bridges to the two imidazolium cations. (b) μ_1-η^1:η^1 coordination mode of SO_4^{2-}.



Scheme 1. The anion exchange reaction between $Zr(OPr)_4$ and [HMIM][HSO_4] in ethanol.

Table 1
The reactions of [HMIM][HSO_4] with metal salts.[a]

[HMIM][HSO_4] + Metal salt $\xrightarrow[\text{ii)recrystaliztion}]{\text{i) EtOH/reflux}}$ Product

Entry	Salts	Product	
Compound **2**	$ZnCl_2$	$(HMIM)_2Zn(SO_4)_2$	
Compound **3**	$MnCl_2$	$(HMIM)_2Mn(SO_4)_2$	
Compound **4**	$Cu(OAc)_2$	$(MIM)_4Cu(HSO_4)_2$	

[a] Metal salt (1 equiv), [HMIM][HSO_4] (2.0 equiv), ethanol as solvent, refluxed for four hours.

by the single-crystal X-ray diffraction method (Fig. 1). Interestingly, $Zr(OPr)_4$ and [HMIM][HSO_4] in ethanol carried out the anion exchange reaction that propoxide groups on $Zr(OPr)_4$ were exchanged by [SO_4^{2-}] to form the zirconium imidazole template sulfate as shown in Scheme 1.

As can be seen from the above results, the reaction of $Ti(O^iPr)_4$ in [HMIM][HSO_4] gave rise to an unknown hydrolysis product, however, the reaction of $Zr(OPr)_4$ led to the formation of imidazole template sulfate via the anion exchange reaction. The design and construction of coordination polymers is of current interest in the fields of supermolecular chemistry and crystal engineering due to their fascinating structure diversities and potential applications as functional materials [10–16]. Particularly, the open-framework sulfates combing transition metals and organic groups have attracted a great interest since Rao et al. reported the first two one dimensional (1D) cadmium sulfates [17–26]. Recently, Kammoun et al. reported the synthesis of imidazole metal sulfates via slow evaporation method in aqueous solution to form zero dimentional structures with a paramagnetic behaviour [27]. To see if our method can be extended to synthesize other imidazole

Table 2
Summary of crystallographic data for **1**–**3**.

Compound	**1**	**2**	**3**	**4**
Chemical formula	$[C_4H_7N_2]_2[Zr(SO_4)_3(C_2H_6SO)_2]$	$[C_4H_7N_2]_2[Zn(SO_4)_2]$	$[C_4H_7N_2]_2[Mn(SO_4)_2]$	$[C_4H_6N_2]_4[Cu(HSO_4)_2]$
M (g mol^{-1})	701.89	423.72	413.29	586.11
Crystal system	triclinic	monoclinic	monoclinic	tetragonal
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P4_2/n$
a (Å)	9.3903(4)	8.8966(8)	8.9645(9)	13.4462(4)
b (Å)	10.9756(4)	9.4753(8)	9.4645(10)	13.4462(4)
c (Å)	13.1648(5)	17.6898(16)	17.7076(18)	13.5775(6)
α (°)	75.0700(10)	90.00	90.00	90
β (°)	81.5880(10)	95.589(2)	95.104(3)	90
γ (°)	81.8360(10)	90.00	90.00	90
V ($Å^3$)	1289.16(9)	1484.1(2)	1496.4(3)	2454.82(18)
Z	2	4	4	4
ρ_{calc} (g/cm^3)	1.808	1.896	1.834	1.586
μ (mm^-1)	0.903	5.413	1.209	1.118
$\boldsymbol{F}(000)$	716.0	864.0	844.0	1212.0
Data/restraints/parameters	4497/0/331	2636/6/211	2640/0/208	3021/24/160
Goodness-of-fit (GOF) on $\boldsymbol{F}^2$	1.048	1.109	1.065	1.054
$R_1[I > 2\sigma(I)]$	0.0285	0.0630	0.0321	0.0576
ωR_2	0.0743	0.1789	0.0906	0.1938