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Solvothermal Synthesis of Nano-Sized Nickel Complex with 1-Methylimidazole Using Ionic Liquid

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One-dimensional nanostructures of nickel complex with 1-methylimidazole $[Ni(C_4H_6N_2)_6(BF_4)_2]$ have been prepared *via* solvothermal route using ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate salt ($[bmim][BF_4]$) as reactive medium. The complex was characterized by elemental analysis, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared absorption spectroscopy, Raman spectra, magnetic measurement and thermal analysis. The SEM and TEM images indicate that the complex is rod-like with diameter of about 180-530 nm and the length of 0.29-2.80 μm. The magnetic measurement exhibits that the complex shows paramagnetic behaviour and its effective magnetic moment is 2.79 B.M.

Key Words: Nanorod, Nickel complex, 1-Methylimidazole, Ionic liquid, Solvothermal route.

INTRODUCTION

With growing concerns over the environmental impact and health hazards of traditional volatile organic solvents, researchers continue to search for green alternatives. Room-temperature ionic liquids, as a new solvent system, have received much attention in many fields of chemistry because of their unique physical and chemical properties, such as high fluidity, high thermal stability, low melting point, extended temperature range in the liquid state, low toxicity, high ionic conductivity and ability to dissolve a variety of chemicals[1-4]. Admirable progress has been made in exploring their applications as green solvents in organic synthesis[5], catalysis[6] and material synthesis[7-12], but the use of ionic liquids in coordination chemistry is still in fancy. Only in recent years, the use of ionic liquids in the synthesis of coordination structures has been gradually explored[13-22]. Xiao *et al.*[15] first reported the *in situ* formation of 1-butyl-3-methylimidazole-2-ylidene (bmiy) complexes of palladium $[Br(\mu\text{-}Br)(bmiy)Pd]_2$ and $[Br_2(bmiy)_2Pd]$ in 1-butyl-3-methylimidazolium bromide ionic liquid. Welton *et al.*[16,17] have studied the *in situ* formation of the mixed

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phosphane imidazolylidene palladium complexes $[(PPh_3)_2Pd(bmimy)X](BF_4)$ at room temperature in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid (where X = Cl, Br). Aggarwal *et al.*[18] have reported unexpected side reaction of imidazole-based ionic liquids in the base-catalyzed Baylis-Hillman reaction. Zaworotko *et al.*[19] synthesized *trans*-$[Fe(1\text{-}Meim)_4F_2]BF_4$ using 1-methylimidazolium tetrafluoroborate ionic liquid as a reactant. Li *et al.*[20] prepared the coordination polymer $[Cu(I)(bpp)]BF_4$ in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid by solvothermal method and found that BF_4^- anions entered the final structure as a charge-compensating species. Gedanken *et al.*[21,22] reported the sonochemical synthesis of $M(II)(1\text{-methylimidazole})_6(B)_2$ (where M = Fe, Ni, B = PF_6, BF_4) using ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium hexafluorophosphate) as solvent.

Recently, transition-metal complexes containing imidazole ring have received much attention because of their potential application in catalysis, metal and alloy corrosion inhibition, electrochromic displays, photovoltaic cells and biomaterials[23-28]. When the size of coordination compounds decreases to nanometer range in at least one dimension, they should display novel or enhanced properties compared to micro-size coordination compounds due to quantum size effect[29]. Although some metal imidazole complexes have been successfully prepared, nanometer scale of complexes is surprisingly sparse. To our best of knowledge, the synthesis of nano-sized transition metal complexes of 1-methylimidazole has not been reported earlier.

$[bmim][BF_4]$, as an ionic liquid, is air and moisture stable, neutral, weakly coordinating and high thermal stability. Both its cation and anion can serve as template or charge compensating group in the synthesis. In addition, its low interface tension can result in high nucleation rates and very small particles are generated which undergo weak Ostwald ripening. These properties make it promising as a green reaction medium for synthesis nanometer scale coordination compounds in the solvothermal reaction.

Herein, we reported the synthesis of the nano-sized nickel complex with 1-methylimidazole by solvothermal methods using 1-butyl-3-methylimidazolium tetrafluoroborate as solvent. The composition and structure of the complex were confirmed on the basis of elemental analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, infrared absorption (IR) spectroscopy, Raman spectroscopy and thermal analysis.

EXPERIMENTAL

1-Methylimidazole ($\geq$ 99 %) was obtained from Shanghai Sanwei Industrial Corporation. 1-Chlorobutane, ammonium tetrafluoraborate and nickel nitrate hexahydrate, sodium hydroxide, toluene, dichloromethane, tetrahydrofuran (THF) and ethanol were purchased from Shanghai Chemical Reagent Corporation. All chemicals were analytical grade and used without further purification except for 1-chlorobutane. Double distilled water was used in all the experiments.

Preparation procedure: 1-Butyl-3-methylimidazolium tetrafluoraborate ([bmim][BF_4]) was synthesized as follow[30]: The 1-butyl-3-methylimidazolium chloride (bmimCl): 1-chlorobutane (1.25 mol) and 1-methylimidazole (1.25 mol) were added in toluene (125 mL). The mixed solutions were refluxed at 74 ºC for 9 h, after which they were cooled to room temperature. The toluene was decanted from the remaining viscous oils. Then, the viscous oils were dispersed in THF to recrystallize. The bmimCl was collected and dried in vacuum at 80 ºC for 3 h.

[bmim][BF_4]: Ammonium tetrafluoraborate (NH_4BF_4, 0.32 mol) was added to a solution of bmimCl (0.32 mol) in dichloromethane and stirred for 48 h. The suspension was filtered to remove the precipitated ammonium chloride and organic phase was distilled to remove the residual solvent and dried in vacuum at 80 ºC for 24 h.

Preparation of nickel complex of 1-methylimidazole: $Ni(NO_3)_2·6H_2O$ (1.74 g) was dissolved in 4 mL distilled water and 1-methylimidazole (2.46 g) were dissolved in 20 mL the ionic liquid [bmim][BF_4], respectively. Then the above two solutions were mixed through adding the $Ni(NO_3)_2$ solution dropwise into [bmim][BF_4] solution containing 1-methylimidazole under stirring. After homogenization of the mixture solution occurred, pH value of the mixture solution was adjusted to 8-9 with aqueous solution of 1 mol/L NaOH. The resultant mixture solution was transferred to a Teflon autoclave and kept in an oven at 150 ºC for 6 h. Then, the autoclave was cooled to room temperature naturally. After the cooled mixture was diluted with ethanol, the products were separated by centrifugation, washed with acetonitrile and ethanol and dried at 60 °C under vacuum. The obtained product was bluish green powder.

Characterization: The morphology of the samples was characterized by JEOL 100CX transmission electron microscope (TEM) and Hitachi S-4300 scanning electron microscope (SEM). TEM samples were prepared by dispersing the sample with ethanol and deposited onto carbon coated copper grids. SEM samples were prepared by dispersing the sample with ethanol and deposited onto crystal silicon. Elemental analysis of complex was carried out with a Vario EL(II) elemental analyzer. X-ray diffraction analysis was performed on a Rigaku D/max-2500 X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ =1.5406 Å). Fourier transform infrared spectroscopy (FT-IR) was conducted at a FTS-40 infrared spectro--scopy. IR spectra of the compounds were obtained by forming thin transparent KBr pellet containing the materials of interests. Raman spectroscopic measurement was carried out at room temperature with Renishaw MKI1000 micro-Raman spectrometer system. The 514.5 nm line of argon ion laser was used as the excitation source. The thermal gravimetric analysis (TG) and derivative thermal gravimetric analysis (DTG) were carried out using a Netzsch STA 409 thermal analysis TG/DTG system. Measurements were made at a heating rate of 5 ºC/min from 25-1200 ºC under nitrogen atmosphere. The magnetic measurement was performed with Lake Shore 7410 vibrating sample magnetometer (VSM) at room temperature.

RESULTS AND DISCUSSION

Composition and structure analysis: Table-1 shows the elemental analysis results.

TABLE-1
ELEMENTAL ANALYSIS OF THE SYNTHESIZED COMPLEX

Complex	C % Found (cal.)	H % Found (cal.)	N % Found (cal.)
$Ni(C_4H_6N_2)_6(BF_4)_2$	39.71 (39.75)	5.03 (5.05)	23.16 (23.19)

Fig. 1 shows the XRD pattern of the complex. The diffraction peaks in this pattern can not be indexed as either $Ni(OH)_2$ or NiO, which was usually prepared by conventional solution-phase method. The result suggests that the Ni^{2+} ions coordinate with 1-methylimidazole ligand rather than OH^- to form a new crystalline complex in this reaction condition. Furthermore, the diffraction peaks are matching very well those of *hexakis*(1-methylimidazole)-nickel(II)*bis*(tetrafluoroborate) $[Ni(C_4H_6N_2)_6(BF_4)]$ complex reported previously[22], confirming that the synthesized complex is properly $[Ni(C_4H_6N_2)_6(BF_4)]$. It belongs to the trigonal space group $p^{\bar{3}}$, with a = 11.1764 Å, c = 7.7657 Å. In this structure, the Ni^{2+} ion is coordinated octahedrally by six equivalent nitrogen atoms of the 1-methylimidazole groups and the two BF_4^- anions balance the positive charge.

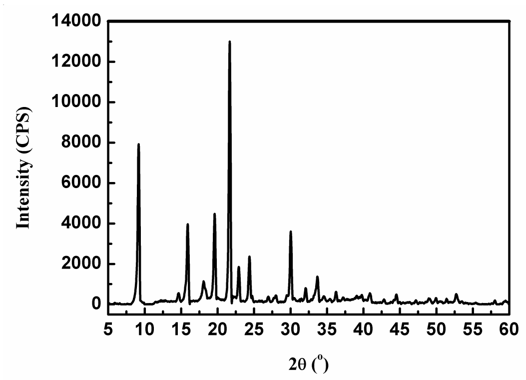


Fig. 1. XRD pattern of the complex

SEM and TEM studies: Fig. 2 shows the SEM (a) and TEM (b) images of the complex. It can be seen that the complexes possess one-dimensional rod-like morphology. The nanorods have diameter ranging from 180-530 nm and length extending from 290-2800 nm. Each nanorod is straight and has un-uniform diameter along its entire length.

IR and Raman spectra: The IR and Raman spectra of the complex are shown in Figs. 3 and 4, respectively. The Raman and IR vibration bands observed in the complex and their proposed assignments are given in Table-2[22,31,32]. The vibration bands assigned to the organic ligand, $C_4H_6N_2$, are shifted, as reported previously by

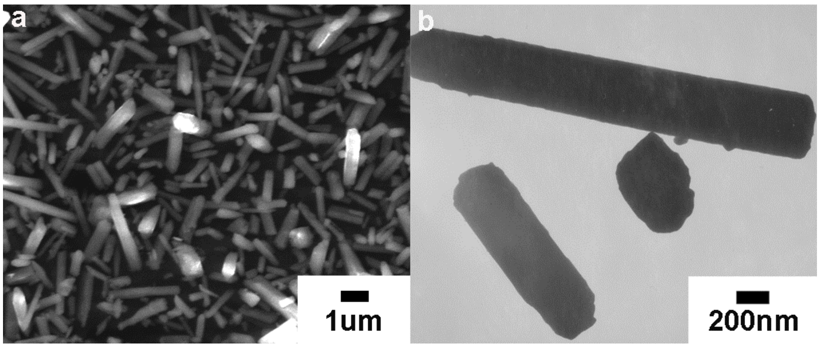


Fig. 2. SEM (a) and TEM (b) image of the complex

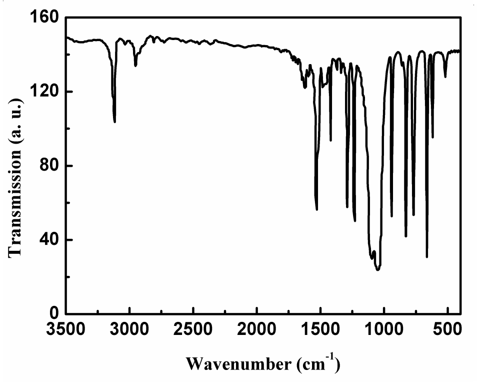


Fig. 3. IR absorption spectra of the complex

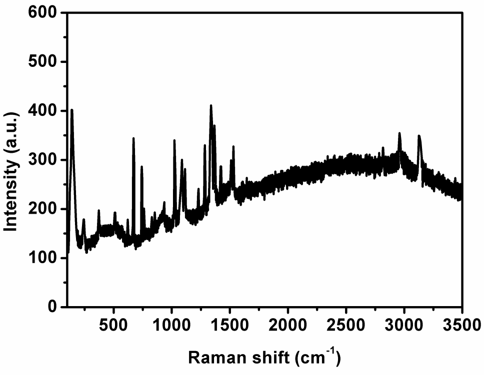


Fig. 4. Raman spectra of the complex

Reedijk[31,32], Perchard and Novak[33]. The Raman bands for Ni-N vibration in the region below 300 cm^{-1} appear and are in accordance with the literature values[34]. The Raman bands at 761, 521 and 377 cm^{-1} are ascribed to the vibration of the BF_4^-[35]. These results strengthen our assignment of the ligands surrounding the central Ni^{2+} ion. The observed vibration bands for the BF_4^- anion confirm that the anion is not bonded to the nickel ion[31,36].

Magnetic measurement: The nickel complexes show the paramagnetic behaviour[31,32], which can be seen in Fig. 5. The measured magnetic moment of the complex $[Ni(C_4H_6N_2)_6(BF_4)]$ is 2.79 B.M. at room temperature. This value is close to the theoretical spin magnetic moment (μ_s) values 2.83 B.M., which is calculated according to the electronic ground-state configurations of Ni^{2+} (d^8) ion in the complexes. The magnetization of the synthesized nickel complexes is unsaturated in the range of the applied magnetic field.

Thermal analysis: The thermal stability of the synthesized complex was examined by the thermogravimetry/derivative thermogravimetry (TG/DTG). Three main stages of weight loss are presents in the TG and DTG profiles of the complex, as shown in Fig. 6. The complex is stable, with a TG plateau, up to 182 ºC where the first releasing step occurs. It is followed by a second process in the temperature

TABLE-2
IR AND RAMAN VIBRATION BANDS (cm^{-1}) FOR THE COMPLEX

Liquid ligand ($C_4H_6N_2$)		$Ni(C_4H_6N_2)_6(BF_4)_2$		Assignments
IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	
3131 w	3128 w	3134 m	3158 m	C-H stretching
3105 m	3103 w	–	–	C-H stretching
3009 sh	3000 w	–	–	–
2986 sh	2951 m	2966 s	2968 m	CH_3 stretchings
2952 m	–	2942 m	2824 w	–
1675 w	–	1651 w	–	Combination bands
1589 w	–	1621 w	–	–
1518 s	1510 s	1532 s	1519 m	Ring stretching (R_1)
1506 sh	1500 w	1519 sh	–	Ring stretching (R_2)
1463 w	1472 w	1481 w	–	CH_3 bending
1421 m	1420 m	1422 s	1426 m	CH_3 bending
1361 w	1353 w	1372 w	–	Ring stretching (R_3)
1328 w	1328 s	1338 w	1339 s,b	Ring stretching (R_4)
1286 s	1288 s	1289 s	1289 s	In-plane C-H bending
1232 vs	1230 s	1243 s	1235 m	Ring stretching (R_5) + C-N stretching
1109 s	1105 w	1112 s,b		In-plane C-H bending
1078 vs	1075 s	1096 s,b	1095 s,b	In-plane C-H bending
1029 m	1025 s	1036 s, b	1029 s	CH_3 deformation + BF_4^- vibration
909 s	904 m	938 s	941 w	Ring stretching (R_6)
860 sh	847 w	859 sh	857 w	Out-of-plane C-H bending
821 s	818 w	827 s	–	Out-of-plane C-H bending
744 s	740 s	776 s	761 s	Out-of-plane C-H bending + BF_4^- vibration
665 vs	665 s	666 s	674 s	Ring stretching and C-N stretching
618 s	616 w	619 s	–	Ring deformation
–	–	522 m	521 w	BF_4^- vibration
355 w	353 w	–	377 m	C-N deformation + BF_4^- vibration
224 w	220 w	–	246 m	C-N deformation
–	–	–	158 s	Ni-N vibration

range 297-453 ºC. The weight loss of the first two stages was approximately 81.9 %, which was assigned to the decomposition of nickel complex of 1-methylimidazole. The third stage from 470-1200 °C, the weight loss was about 7.2 %, which was attributed to further oxidation of residual component. The residual component is black powder and may be nickel oxide (measured 10.9 %, calculated 10.4 %). To investigate this point further, a sample of $[Ni(C_4H_6N_2)_6(BF_4)]$ was placed in a tube furnace at 1200 °C for 1 h under N_2. After the sample cooled, XRD analysis on the sample indicated the presence of NiO. Given this information, the residual component in the TGA experiment corresponds to NiO.

Formation mechanism: Following conventional solution-phase reaction, it is assumed that the first stage of the current reaction involves the dissociation of $Ni(NO_3)_2$ to Ni^{2+} and NO_3^-. Then, the competitive coordination process of Ni^{2+} with

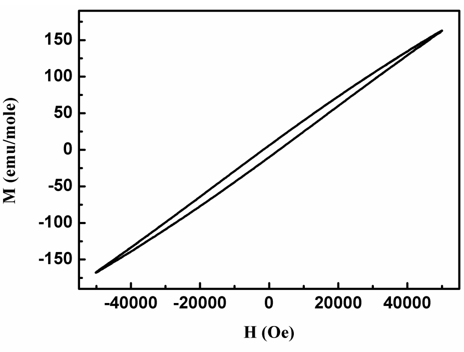


Fig. 5. Magnetization curve of the complex at room temperature

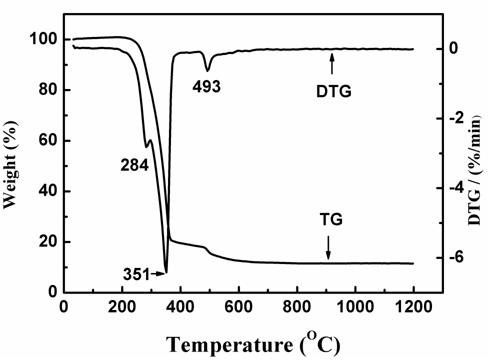
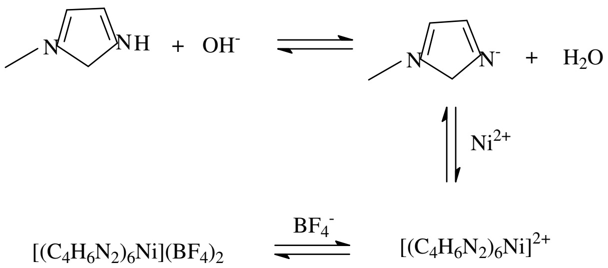


Fig. 6. TG and DTG of the complex

nitrogen atoms of the imidazole ring and oxygen atom of OH^- appears. In order to investigate the effects of ionic liquid on competing reaction for Ni^{2+} between nitrogen atoms of the imidazole ring and OH^-, we designed and conducted several controlled experiments by varying volume ratio of ionic liquid to water (v_{IL}/v_{H_2O}) under same conditions. The first experiment conducted at $v_{IL}/v_{H_2O} = 0$ (without [bmim][BF_4]) gave an β-$Ni(OH)_2$ product. The second experiment conducted at $v_{IL}/v_{H_2O} = 0.5$ also yielded mainly β-$Ni(OH)_2$. The third experiment was made at $v_{IL}/v_{H_2O} = 1$ and the products were mixture of [$Ni(C_4H_6N_2)_6(BF_4)$] and β-$Ni(OH)_2$. With further increasing volume ratio of ionic liquid to water up to 2, the products were mainly $Ni(C_4H_6N_2)_6(BF_4)$]. These results indicate that the amount of [bmim][BF_4] in reaction solution affects the competing reaction for Ni^{2+} between nitrogen atoms of 1-methylimidazole and oxygen atom of OH^-. When the volume ratio of [bmim][BF_4] to water increased, the coordination ability of 1-methylimidazole was gradually strengthened and that of OH^- was gradually weakened because the [bmim][BF_4] made surrounding environment of Ni^{2+} different from that in conventional aqueous solution and prevented competitive reaction of OH^- with Ni^{2+}. Thus, 1-methylimidazole preferred to coordinate with nickel ion under the current experimental condition. Our first assumption is, following earlier reports, that the ionic liquid is the source of the imidazole ring[15-19] and the counter ion (BF_4^-) in the product[20-22,37], while losing a butyl group during the reaction. However, [bmim][BF_4] is thermally stable at 309 ºC and decomposed completely at 528 ºC[22,30,38], confirming that the ionic liquids are stable at the reaction temperature, Without any decomposition and losing either methyl or butyl group[39]. A controlled experiment was conducted under the same condition except for the absence of 1-methylimidazole. The product was green powder, which was identified as NiOH by XRD. This means that the 1-methylimidazole source is not the ionic liquid, but the reactant 1-methylimidazole. Conversely, the anions in the product originate from the ionic liquid. The possible reaction process is described in **Scheme-I**.



Scheme-I: Illustration of reaction process

When sodium hydroxide was added to the solution, 1-methylimidazole reacted with hydroxyl and lost its proton hydrogen. Then, 1-methylimidazole converted it to the 1-methylimidazole with a nitrogen atom bearing negative charge, which is preferentially coordinated to the central Ni^{2+} ion. Each Ni^{2+} ion is coordinated octahedrally by six 1-methylimidazole molecules and BF_4^- anions entered the final structure as a charge compensating species and formed salt.

Conclusion

In summary, we have explored the use of an ionic liquid [Bmim][BF_4] as a thermally stable solvent in the solvothermal synthesis of nanostructure coordination compound $Ni(C_4H_6N_2)_6(BF_4)_2$. In this synthesis reaction, 1-methylimidazole preferred to coordinate with Ni^{2+} ion and each Ni^{2+} ion is coordinated octahedrally by six 1-methylimidazole molecules. BF_4^- acts as charge-stabilizing agent in the formation of salt. The morphology of complex $Ni(C_4H_6N_2)_6(BF_4)_2$ is rod-like with diameter ranging from 180-530 nm and length extending from 290-2800 nm. The measured magnetic moment of the $[Ni(C_4H_6N_2)_6(BF_4)]$ is 2.79 B.M. This study demonstrates that ionic liquids, with their superior properties, may be promising for use as new type of clean and effective solvent in the preparation of nanometer scale transition-metal coordination compounds.

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