

Ionothermal synthesis and structural characterization of $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Br}_2$ and $[\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Br}_2$

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Abstract. The ionothermal synthesis and spectroscopic, thermal and structural characterization of two new compounds $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Br}_2$ (**1**) and $[\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Br}_2$ (**2**) [$(\text{C}_4\text{H}_6\text{N}_2) = \text{N}$ -methylimidazole] are reported. In both **1** and **2**, the central metal Cu (or Ni) ion adopts a square planar geometry and is bonded to the N-atoms of four terminal N-methylimidazole ligands.

Keywords. Ionothermal technique; ionic liquid; single crystal; crystal structure.

1. Introduction

The hydrothermal technique is originally the domain of geochemists and mineralogists having interest in simulating mineral formation. In fact, the hydrothermal technique may be regarded as a special case of a chemical transport reaction.^{1–5} However, some disadvantages were observed from the investigation of the solid-state synthetic methods at an intermediate temperature. The search for alternatives to common solvents for the solvothermal synthesis is one of the most challenging issues in the materials science.

Ionic liquids comprised of only ions in liquids at low temperature ($< 100^\circ\text{C}$) and possess a wide range of liquid properties, negligible vapor pressure, high electrical conductivity and wide electrochemical windows, high solvability and excellent thermal and chemical stability.^{6–8} These characteristics of the ionic liquids may make them potential media for the preparation of inorganic and inorganic-organic hybrid materials. This process of using ionic liquid as both the solvent and potential template or structure directing agent in the formation of solids is termed as ionothermal synthesis.⁹ Recently, some compounds containing both borate and phosphate such as BaBPO_5 and $\text{C}_{15}\text{H}_{40}\text{BCO}_2\text{N}_{30}\text{O}_{16}\text{P}_3$ have been synthesized by a high-temperature synthesis in molten salts and low temperature-high pressure approaches by ionothermal technique.^{10–14} Ni(II) and Cu(II) have been the most widely investigated species

for several reasons: (i) they are often very effective as a templating agent in many synthesis, (ii) their complexes display unusually high solution stability and (iii) Ni^{2+} can exist in either high-spin or low-spin form according to the ligand's structural features. A large number of tetraaza macrocyclic ligands and their complexes have been synthesized and studied.^{15,16}

Here, we wish to report two new Cu(II) and Ni(II) complexes coordinated by four N-methylimidazole ligands $\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Br}_2$ (**1**) and $\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Br}_2$ (**2**) that are synthesized using ionic liquid as a medium. Although several complexes of copper with N-methylimidazole (or 4-methylimidazole) and halogen ligands have been reported,^{17–19} they are quite different from **1** and **2** in terms of their structures.

2. Experimental

2.1 Synthesis of the compounds

All reagents were purchased commercially and used without further purification and all manipulations were performed in air.

Procedure for synthesis of **1**: 4.5 mg (0.018 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1.0 g (4.57 mmol) of 1-butyl-3-methylimidazolium bromide (bmimBr) was sealed in a thick-walled Pyrex tube, and then the tube was put in an oven. The reaction was carried out at 110°C for 24 h to afford dark blue crystals of $\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Br}_2$ (**1**) in about 40.7% yield. Pure crystals were obtained by

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acetone washing. Elemental analysis: calc. C 34.78, H 4.35, N 20.29 (%); found C 34.4, H 4.05, N 19.50 (%).

Synthesis of **2**: 4.8 mg (0.024 mmol) of $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, 1.3 g (5.94 mmol) 1-butyl-3-methylimidazolium bromide (bmimBr) was sealed in a thick-walled Pyrex tube. And then the tube was put in an oven. The reaction was carried out at 110°C for 24 h to afford purple crystals of $\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Br}_2$ (**2**) in about 47.3% yield. Pure crystals were obtained by acetone washing. Elemental analysis: calc. C 35.10, H 4.39, N 20.48 (%); found: C 34.95, H 4.35, N 20.41(%).

2.2 X-ray single-crystal diffraction

The crystal data of **1** and **2** were collected on a Bruker SM ART CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 and 293K, respectively. The structures were solved by the direct methods and difference Fourier map with SHELXL-97 program, and refined by full-matrix least-squares techniques on F^2 . Anisotropic thermal parameters were used to refine non-hydrogen atoms. Hydrogen atoms on C and N atoms of the organic ligands were included in their calculated positions. Hydrogen atoms attached to hydroxyl group were found from the difference Fourier maps. A summary of crystal data and structure refinement for compounds **1** and **2** were provided in table 1.

2.3 IR spectrum, TG and elemental analysis

IR spectra were recorded in the range of 4000–400 cm^{-1} on vertex 80 infrared spectrometer (Bruker Company) with pressed KBr pellets. Thermogravimetric analyses (TGA) were recorded on Perkin-Elmer DTA 1700 differential thermal analyzer in a dynamic nitrogen atmosphere with a heating rate of 10°C/min. Elemental analysis was performed on Perkin-Elmer 2400 Analyzer.

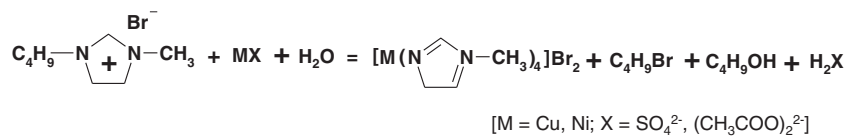
3. Results and Discussion

3.1 Synthesis of compounds **1** and **2**

The reaction sequence for the synthesis of **1** and **2** is shown in scheme 1. As shown in the Scheme, metal cations Cu^{2+} or Ni^{2+} in hydrated metal salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ interact with N atom linked by butyl group in bmimBr ionic liquid to form complex cations $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4]^{2+}$ and $[\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4]^{2+}$. Meanwhile butyl group from the imidazolium species leaves as bromobutane, and other part of the molecule reacts with water to form butanol and H^+ . The H^+ further combines with SO_4^{2-} or CH_3COO^- to generate the corresponding acid. Besides, the results of XRD (figures S1 and S2) and Elemental analysis

Table 1. Crystal data and structure refinement.

	$\text{C}_{16}\text{H}_{24}\text{Br}_2\text{N}_8\text{Cu}$	$\text{C}_{16}\text{H}_{24}\text{Br}_2\text{N}_8\text{Ni}$
formula weight	551.78	546.92
temperature, K	296(2)	293(2)
wavelength, \AA	0.71073	0.71073
crystal system	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/c
a, \AA	7.635(2)	7.6103(6)
b, \AA	9.377(2) A	9.3605(7)
c, \AA	15.006(4)A	16.5573(10)
α , deg	90	90
β , deg	92.365(3)	114.981(3)
γ , deg	90	90
volume, \AA^3	1073.4(5)	1069.14(14)
Z	2	2
Dc, mg/m^3	1.707	1.699
μ (Mo $\text{K}\alpha$), mm^{-1}	4.758	4.663
F (000)	550.0	548.0
Data/restraints/parameters	2613/ 0 / 126	2648 / 0 / 126
Collected/unique [R_{int}]	7908 / 2662 [0.0374]	7865 / 2665 [0.0174]
Index ranges	$-9 \leq h \leq 10, -12 \leq k \leq 12,$	$-10 \leq h \leq 10,$
GOF on F2	1.035	1.027
final R1, wR2 [$I > 2\sigma(I)$]	0.0375, 0.0914	0.0381, 0.1000
R1, wR2 (all data)	0.0677, 0.1014	0.0548, 0.1102
Largest diff.peak / hole ($e \cdot \text{\AA}^{-3}$)	0.851, -0.731	0.888, -1.277



Scheme 1. Reaction sequence for the synthesis of two compounds.

indicate that the two compounds **1** and **2** possess very high phase purity.

3.2 Structure of crystal and molecule of 1 and 2

The ORTEP view of the complex **1** with the atomic numbering scheme and packing of the compound in the unit cell are shown in figures 1 and 2, respectively. The selected bond lengths and bond angles are listed in table 2. The crystal structure of **1** is built up from copper complex cation $Cu(C_4H_6N_2)_4^{2+}$ and two bromide anions. The Cu^{2+} in the isolated $Cu(C_4H_6N_2)_4^{2+}$ cation is coordinated by four N atoms of the N-methylimidazole ligands within a slightly distorted square-planar arrangement with Cu-N bond lengths of 2.007 and 2.026 Å, respectively. That is, the bond lengths of Cu-N₁ and Cu-N_{1A} are equal (2.007 Å), so are the two bond lengths of Cu-N₂ and Cu-N_{2A} (2.026 Å), as shown

in figure 1. The bonding angles N₁-Cu-N_{1A} = N₂-Cu-N_{2A} = 180.00°, N₁-Cu-N_{2A} = N₂-Cu-N_{1A} = 90.52° and N₁-Cu-N₂ = N_{1A}-Cu-N_{2A} = 89.48°, respectively, indicate that the two coupled bonds N₁-Cu-N_{1A} and N₂-Cu-N_{2A} are almost orthogonal. Besides, the sum of all the angles of five-member ring comprised of N-methylimidazole is 540° since the five inner angles formed by N₂-C₇-N₄-C₁₀-C₉ (figure 1) are 105.2, 111.0, 107.6, 106.1 and 110.1°, respectively. This finding indicates that imidazole rings are all planar in the compound **1**. As seen from figure 2, the Br atoms are far away from the central Cu cation or other atoms; no bond has been formed between Br and any other atom. This is very different from the compound $[CuBr_2(C_4H_6N_2)_4]$ reported by Näther *et al.*¹⁸ In $[CuBr_2(C_4H_6N_2)_4]$, Cu-Br distance is determined to be 3.2371 Å, indicating that a long contact between Cu and Br has been generated. The structure of crystal **2** is very similar to **1** according

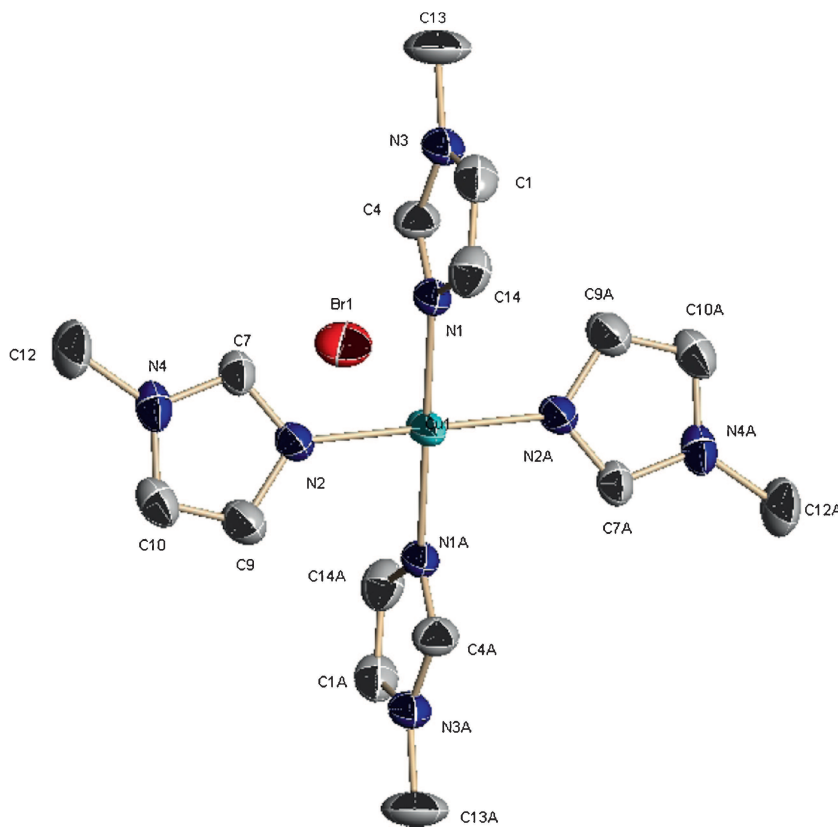


Figure 1. ORTEP view of the basic units in compound **1**. Symmetry codes: 'x, y, z', '-x+1/2, y+1/2, -z+1/2'; '-x, -y, -z'; 'x-1/2, -y-1/2, z-1/2'.

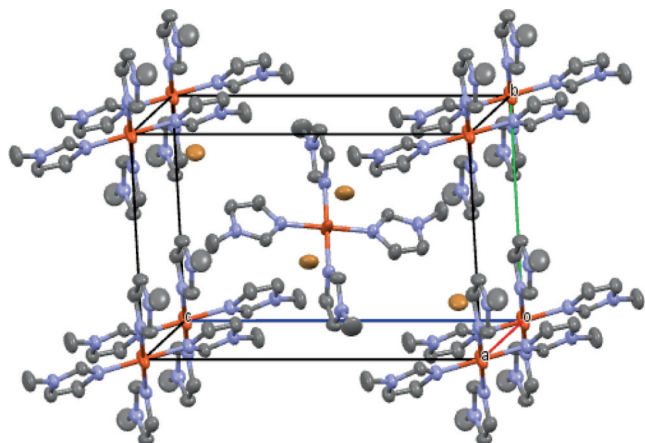


Figure 2. Packing of the compound **1** in the unit cell.

Table 2. Selected bond lengths (Å) and angles (°) of compound **1** and **2**.

Bonds	Lengths/Angles
Cu(1)-N(1)	2.007(2)
Cu(1)-N(2)#1	2.026(2)
Cu(1)-N(1)#1	2.007(2)
Cu(1)-N(2)	2.026(2)
Ni(1)-N(1)	2.004(2)
Ni(1)-N(3)#1	2.026(2)
Ni(1)-N(1)#1	2.004(2)
Ni(1)-N(3)	2.026(2)
N(1)-Cu(1)-N(1)#1	180.0
N(1)#1-Cu(1)-N(2)#1	89.48(10)
N(1)#1-Cu(1)-N(2)	90.52(10)
N(1)-Cu(1)-N(2)#1	90.52(10)
N(1)-Cu(1)-N(2)	89.48(10)
N(2)#1-Cu(1)-N(2)	180.000(1)
N(1)-Ni(1)-N(1)#1	180.000(2)
N(1)#1-Ni(1)-N(3)#1	90.64(10)
N(1)#1-Ni(1)-N(3)	89.36(10)
N(1)-Ni(1)-N(3)#1	89.36(10)
N(1)-Ni(1)-N(3)	90.64(10)
N(3)#1-Ni(1)-N(3)	180.000(1)

to figures S3 and S4 and table 2, even though some cell parameters are different from each other.

3.3 IR spectra

Compound **1** and **2** have the same organic ligands, so their IR spectra are basically same. As seen from the spectrum (figure S5a), the absorption bands observed at 3429.4 and 3378.1 cm^{-1} may be ascribed to stretching vibration of C-H bonds in imidazole ring. The other bands at 3106.2, 2948.21 and 1630.1 cm^{-1} are identified to be stretching and bending vibration of

C-H bonds in methyl groups. Similarly, the bands at 3337.1, 3291.2 and 3246.8 cm^{-1} likely belong to stretching vibration of C-H bonds in imidazole ring, which is basically in agreement with the spectrum of N-methylimidazole (figure S6). Moreover, the absorption band at 3480.7 cm^{-1} is attributable to the stretching vibration of O-H bond in H_2O absorbed from air (figure S5b), which is in agreement with the result obtained by TG curve of **2**. Also, the absorption bands at 3166.7, 2947.1, 2887.6 and 1633.5 cm^{-1} are relevant to the stretching and bending vibration of C-H bonds in methyl groups.

3.4 Thermal analysis

It is shown in figure 3 that the TG curve of compound **1** includes a one step mass loss. The mass loss in the temperature range from 110 to 430°C is 75.49%, which is attributed to the continuous release of four N-methylimidazoles $\text{C}_4\text{H}_6\text{N}_2$ and one Br in the crystal. This is basically in accord with the theoretical calculation value 73.94%. Diversely, TG curve of **2** displays three steps of mass loss. The first one from 52 to 104°C is likely to be the release of adsorbed water (8.55%) and not crystal water because the temperature of the complete loss of water is close to 104°C, showing that the interaction between water molecule and the crystal is very weak. Furthermore, the molecular formula of the hydrated compound $[\text{Ni}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Br}_2 \cdot 8\text{H}_2\text{O}$ is inconsistent with the results of the elemental analysis listed in Section 2.1. The second mass loss of about 14.51% from 210 to 255°C corresponds to the elimination of one Br, which is in accordance with the theoretical calculation value of 14.63%, while the third one of about 59.32% from 294 to 366°C is identified to be the release

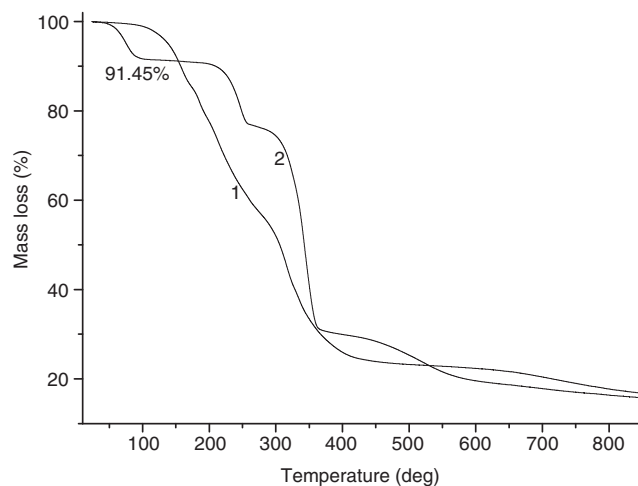


Figure 3. The TG curve of compound **1** and **2**.

of four N-methylimidazoles $C_4H_6N_2$, agreeing with the theoretical value of 59.97%. These results indicate that the compounds **1** and **2** possess good thermal stability below 110 and 210°C, respectively.

4. Conclusions

Two novel complexes are ionothermally synthesized in an ionic liquid and characterized by X-ray single crystal diffraction, FT-IR, TGA and elemental analysis. Comparing compound **1** with **2**, their similarity in the structure is as follows: (1) the two cations, Cu^{2+} or Ni^{2+} are coordinated by four N-methylimidazole ligands; (2) they both belong to monoclinic system; (3) the coordination bond lengths of Ni-N and Cu-N in **1** and **2** are almost equal to the four Ni-N bond lengths 2.004 and 2.026 Å, and four Cu-N bond lengths 2.007 and 2.026 Å, respectively. Moreover, metal cation and N atoms in imidazole rings are all planar, so are the imidazole rings.

Supplementary Information

CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 1006606 for **1** and 1006607 for **2**, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif. The ORTEP view of **2**, packing of **2** in the unit cell, FT-IR spectra, XRD patterns and selected bond lengths (Å) and angles (°) of **1** and **2** are included in supplementary file available at www.ias.ac.in/chemsci.

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