



# Non-covalent interactions in 2-methylimidazolium copper(II) complex (MeImH)<sub>2</sub>[Cu(pfbz)<sub>4</sub>]: Synthesis, characterization, single crystal X-ray structure and packing analysis



Raj Pal Sharma<sup>a,\*</sup>, Anju Saini<sup>a</sup>, Santosh Kumar<sup>a</sup>, Jitendra Kumar<sup>a</sup>, Ranganathan Sathishkumar<sup>b</sup>, Paloth Venugopalan<sup>a,\*\*</sup>

<sup>a</sup> Department of Chemistry, Panjab University, Chandigarh, 160014, India

<sup>b</sup> Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012, Karnataka, India

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## ABSTRACT

A new anionic copper(II) complex, (MeImH)<sub>2</sub>[Cu(pfbz)<sub>4</sub>] (**1**) where, MeImH = 2-methylimidazolium and pfbz = pentafluorobenzoate has been isolated by reacting copper(II) sulfate pentahydrate, pentafluorobenzoic acid and 2-methylimidazole in ethanol: water mixture in 1:2:2 molar ratio. This complex **1** has been characterized by elemental analysis, thermogravimetric analysis, spectroscopic techniques (UV-Vis, FT-IR) and conductance measurements. The complex salt crystallizes in monoclinic crystal system with space group C2/c. Single crystal X-ray structure determination revealed the presence of discrete ions: [Cu(pfbz)<sub>4</sub>]<sup>2-</sup> anion and two 2-methylimidazolium cation (C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>)<sup>+</sup>. The crystal lattice is stabilized by strong hydrogen bonding and F⋯F interactions between cationic-anionic and the anionic-anionic moieties respectively, besides π-π interactions.

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## 1. Introduction

Supramolecular interactions of aromatic systems have attracted considerable attention during the last decade [1–6] because of the utilization of weak intermolecular contacts (non-covalent interactions) for the design and development of novel functional materials. The topology and architecture depends upon choice of metal ions and ligands [7–9]. Weak intermolecular interactions involving fluorine atoms are significant in diverse fields such as drug design, protein structure and crystal engineering [10].

Complexes of 2-methylimidazole (MeIm) with transition metal ions have attracted great importance because of their biological and pharmaceutical activities such as antiviral, antimicrobial, antifungal and antimycotic, antihistaminic, antiallergic anthelmintic and antimetastatic properties [11–14]. The biological role of

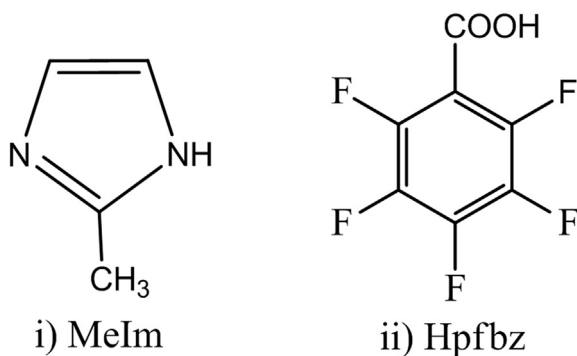
complexes containing an imidazole ring system can be connected with the two N atoms, which have different properties; the imino N atom can coordinate with a transition-metal ion, whereas the protonated N atom participates in hydrogen bonding, so they can be used to build desired topologies through C–H⋯F, N–H⋯F interactions [15]. On the other hand, extensive studies on organic fluorine demonstrate that organic fluorine can provide weak but directional C–H⋯F–C interactions between adjacent molecules to generate an expansion of supramolecular architecture [16]. Fluorinated benzoic acids have been used as water tracers in ground and soil water applications and in petroleum reservoirs. With increase in number of fluorine atoms in a benzene ring its toxicity and physiological activities get decreased [17].

The anion pentafluorobenzoate is of interest i) as it has no hydrogen in the core which may facilitate its role as an acceptor of C–H⋯F interactions, ii) can exhibit various coordination modes iii) catalytic role of its complexes in organic transformations [18] and iv) for promising photophysical properties of its lanthanide complexes [19,20]. Therefore, complexation of pentafluorobenzoic acid and 2-methylimidazole with copper metal ion becomes important as copper is an essential trace metal ion present in human body. The

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [rpsharma@pu.ac.in](mailto:rpsharma@pu.ac.in) (R.P. Sharma), [venugopalan@yahoo.com](mailto:venugopalan@yahoo.com) (P. Venugopalan).



**Scheme 1.** Ligands used in synthesis of complex **1** i.e. i) MeIm = 2-Methylimidazole, ii) Hpfbz = 1,2,3,4,5-pentafluorobenzoic acid.

ligands used in the synthesis of complex **1** are shown in [Scheme 1](#). Copper(II) arylcarboxylate and 2-methylimidazole complexes are also of immense importance in chemistry, biology and medicine. However, research on monomeric complexes of copper(II) having benzoic acids and imidazole is limited. Although, the existence of copper(II) anionic complexes is reported in literature but these complexes are rare as copper(II) ion generally exists in the form of neutral or cationic complexes [21]. To the best of our knowledge, this is first structural report of any anionic copper(II) arylcarboxylate complex. Inspired by this, we tried to design/synthesize a monomeric copper complex using pentafluorobenzoic acid and 2-methylimidazole as nitrogen donor ligand as a part of our research interest on copper(II) arylcarboxylate with various N-donor ligands [22–27]. Herein, we report the synthesis, characterization and crystal structure of a novel salt containing rare anionic complex of copper(II),  $(\text{MeImH})_2 [\text{Cu}(\text{pfbz})_4]$ .

## 2. Experimental

### 2.1. Materials and methods

Analytical grade reagents were used throughout this work without any further purification. Elemental analysis was performed using an automatic Perkin Elmer 2400 CHN element analyzer and copper was determined by standard literature methods [28]. Fourier transform infrared spectra (FT-IR) were recorded (neat) on PERKIN ELMER SPECTRUM RX FT-IR system. UV-visible spectra were recorded using HITACHI 330 SPECTROPHOTOMETER. Thermogravimetric analysis (TGA) was done in inert atmosphere using SDT Q600 instrument. The samples contained in alumina pan were heated from 25 °C to 800 °C at a constant rate of 10 °C min<sup>-1</sup> under nitrogen environment with flux (flow rate) of 10 mL/min. The magnetic measurements were carried out using the Gouy's method. The specifications of apparatus used for magnetic measurements were as: Pole face diameter: 10.2 cm; Pole gap: 4.0 cm; Current: 7.0 amp; Magnetic field: 6 kG. The calibrant employed was Hg [Co(SCN)<sub>4</sub>] for which the magnetic susceptibility was assumed to be  $1.644 \times 10^{-5} \text{ cm}^{-3} \text{ g}^{-1}$  at room temperature. All the measured susceptibility values were corrected for diamagnetism of the constituent atoms using the Pascal's constants [29–31]. Magnetic moment was calculated according to the equation:

$$\mu = 2.83(\chi_{\text{mT}})^{1/2}.$$

### 2.2. Synthesis

#### 2.2.1. Synthesis of $(\text{MeImH})_2 [\text{Cu}(\text{pfbz})_4]$ , **1**

0.5 g (2 mmol) of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 0.33 g (4 mmol) of 2-methylimidazole and (4 mmol) 0.85 g of pentafluorobenzoic acid was dissolved in ethanol-water (1:1) mixture. On addition of 0.16 g (4 mmol) NaOH resulted in light blue suspension. The suspension was stirred for half an hour and filtered. Blue colored crystals of complex **1** appeared after 15 days as a result of slow evaporation of mother liquor. The newly synthesized crystals were soluble in water and methanol. The melting point for complex **1** was observed at 182 °C (decomposition). Anal Calcd  $(\text{MeImH})_2 [\text{Cu}(\text{C}_6\text{F}_5\text{COO})_4]$ , Cu = 5.91, C = 46.92, H = 1.30, N = 5.21; found Cu = 5.90, C = 46.78, H = 1.35, N = 5.28. FT-IR (neat, cm<sup>-1</sup>) 3124, 3004, 2934, 1633, 1391, 533, 474. UV-Vis ( $\lambda_{\text{max}}$  = 268 nm, 805 nm and 1010 nm)

### 2.3. Single crystal X-ray determination

The data of 180 frames were collected in Bruker SMART APEX three circled single crystal diffractometer equipped with CCD detector, with the  $2\theta$  fixed at  $-25^\circ$  and a  $\omega$  scan width of  $-1^\circ$ . The frames were then processed using SMART [32], and the spots were analyzed using RLATT [32] to determine the unit cell dimensions. The indexed reflections correspond to the monoclinic crystal system. Data were collected on three sets of 606 frames with  $2\theta = -25^\circ$  and with  $\phi$  values of  $0^\circ$ ,  $90^\circ$ , and  $180^\circ$  respectively. The crystal structure was solved and refined using program package SIR92 [33] and SHELXL [34].

## 3. Results and discussions

### 3.1. Synthesis

The complex **1** was synthesized by using solution phase synthesis using pentafluorobenzoic acid, 2-methylimidazole and copper sulphate pentahydrate in ethanol: water mixture as described in experimental section. The synthetic route for **1** is given in [Scheme 2](#). Surprisingly, instead of  $[\text{Cu}(\text{pfbz})_2 (\text{MeIm})_2]$  (which was expected in analogy with  $[\text{Cu}(\text{pfbz})_2 (\text{Im})_2]$  [35]); an unexpected copper(II) benzoate complex,  $(\text{MeImH})_2 [\text{Cu}(\text{pfbz})_4]$  was isolated. The composition of the synthesized copper(II) complex was established by elemental analyses as given in experimental section and subsequently confirmed by single crystal X-ray structure investigation.

### 3.2. Spectroscopic characterization

The newly synthesized complex **1** has been characterized by FT-IR and UV-Vis spectroscopy. Infrared spectrum of complex **1** (neat) was recorded in the region 4000–400 cm<sup>-1</sup> and tentative band assignments have been made on the basis of earlier reports in literature [36–40]. The infrared spectrum of the complex ([Fig. 1](#)) shows bands at 3124, 3004, 2934 cm<sup>-1</sup> which may be attributed to the  $\nu(\text{N-H})$  and  $\nu(\text{C-H})$  vibrations of the cationic groups. The bands at 1633 and 1391 cm<sup>-1</sup> are ascribed to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$ . The separation  $\Delta\nu = 242 \text{ cm}^{-1}$  between the  $\nu_{\text{as}}(\text{COO})$ - $\nu_{\text{sym}}(\text{COO})$  frequencies in the title complex salt is greater than that of sodium pentafluorobenzoate (210 cm<sup>-1</sup>) suggesting monodentate coordination mode of pentafluorobenzoate (pfb) moieties in title copper pentafluorobenzoate complex. The bands at 533, 474 cm<sup>-1</sup> may be attributed to metal-oxygen and metal-nitrogen stretching vibrations, respectively, in the complex. The peak assignments have been made in consultation with the reported literature values.

The solution state electronic spectrum of the complex in water

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