

## MOLECULAR, CRYSTAL STRUCTURE AND HIRSHFIELD ANALYSIS OF TETRAKIS (2-PROPOXY ISOBUTYL ISONITRILE) COPPER(I) TETRAFLUOROBORATE BY POWDER X-RAY DIFFRACTION STUDY

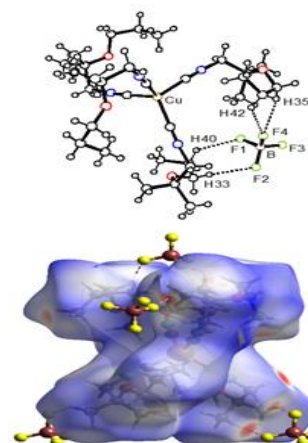
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The molecular and crystal structures of tetrakis (2-propoxy isobutyl isonitrile) copper(I) tetrafluoroborate  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  were confirmed by powder X-ray diffraction study. The preparation and spectroscopic identification were previously reported. The molecular structure displays the distinctive cation  $[\text{Cu}(\text{PIBI})_4]^+$  and anion  $[\text{BF}_4]^-$ . The Cu(I) center of  $[\text{Cu}(\text{PIBI})_4]^+$  unit is surrounded by four 2-propoxy isobutyl isonitrile ligands (each via its isonitrile C atom) assuming a typical tetrahedral geometry. The isonitrile C atoms are covalently bonded to Cu center with a mean bond distance of 1.963(7) Å and C-Cu-C angle of 109.4(4)°. The mean C≡N distance (1.138(9) Å) and rather linear of Cu-C≡N angles (the largest Cu-C-N angle is 177.8(6)° and the smallest angle is 173.9(0)° give a strong indication that the C≡N bond order of 3 in the complex  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ . The counter-ion  $\text{BF}_4^-$  has almost an ideal tetrahedral geometry with an average B-F bond distance of 1.350(4) Å. The crystal packing is achieved by C—H...F short contacts, where each individual  $[\text{BF}_4]^-$  anion is involved symmetrically by its four F atoms with four different surrounding  $[\text{Cu}(\text{PIBI})_4]^+$  cations to form supramolecular three-dimensional network. A Hirshfeld surface analysis was carried out to investigate the intermolecular interactions.



### INTRODUCTION

Isonitriles<sup>1–3</sup> have received a considerable attention in organic chemistry and as ligands in coordination chemistry.<sup>4–11</sup> In general, isonitriles are unstable volatile compounds, they rapidly decompose by oxidation or polymerization and they have also unpleasant odors. Therefore isonitriles are generally converted into isonitrile metal complexes in order to be stabilized and to get rid of their ugly scent,<sup>1,4,12</sup> which can be used

on demand as a source for isonitrile ligand. The isonitrile Cu(I) complex  $[\text{Cu}(\text{MIBI})_4]\text{BF}_4$  (MIBI = 2-methoxyisobutyl isonitrile) (Fig 1), is an intermediate in preparing <sup>99m</sup>Tc-MIBI kits for diagnostic cardiac application in nuclear medicine.<sup>13–15</sup> The tri-coordinated complex  $[\text{Cu}(\text{MIBI})_3][\text{BF}_4]$ , was also reported, in which the Cu center lies on threefold axis and is bonded to three MIBI ligands in a perfect trigonal-planar coordination.<sup>16</sup> Furthermore, different hexa-coordinated carbonyl MIBI complexes of Mn and

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Re were lately reported and their CO releasing, cytotoxicity and antimicrobial properties were carried out.<sup>17</sup> Previously, the synthesis and spectroscopic characterizations of the MIBI analogous, 2-Propoxy Isobutyl Isonitrile (PIBI)

and its Cu(I) complex  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  (Scheme 1) were reported by us.<sup>18</sup> In this article we will present the crystal and molecular structure determination of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  by powder X-ray diffraction study.

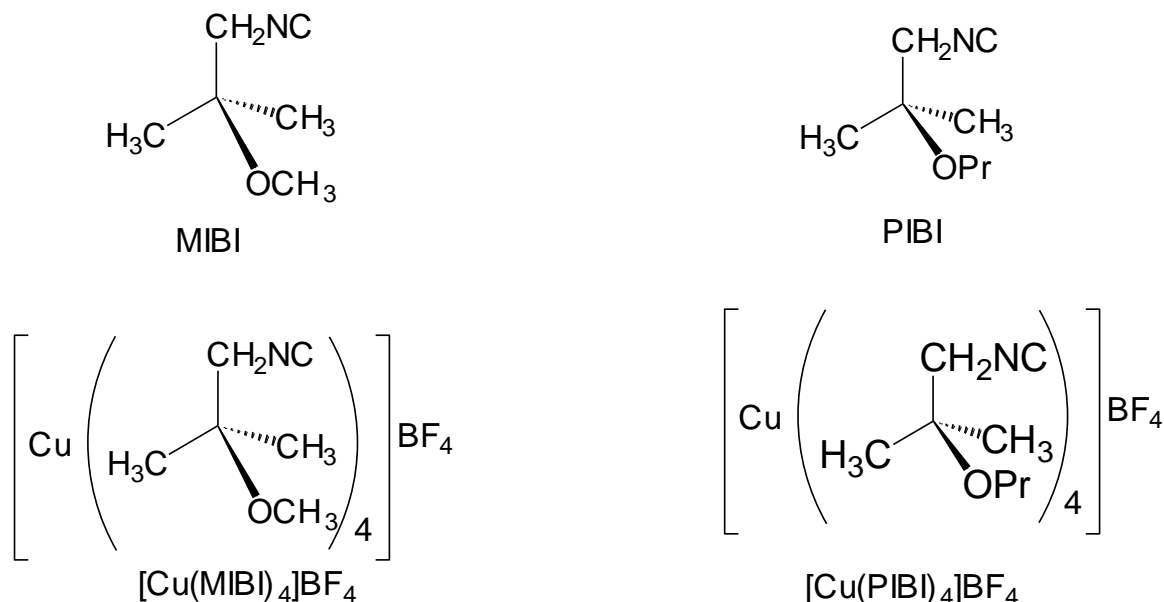
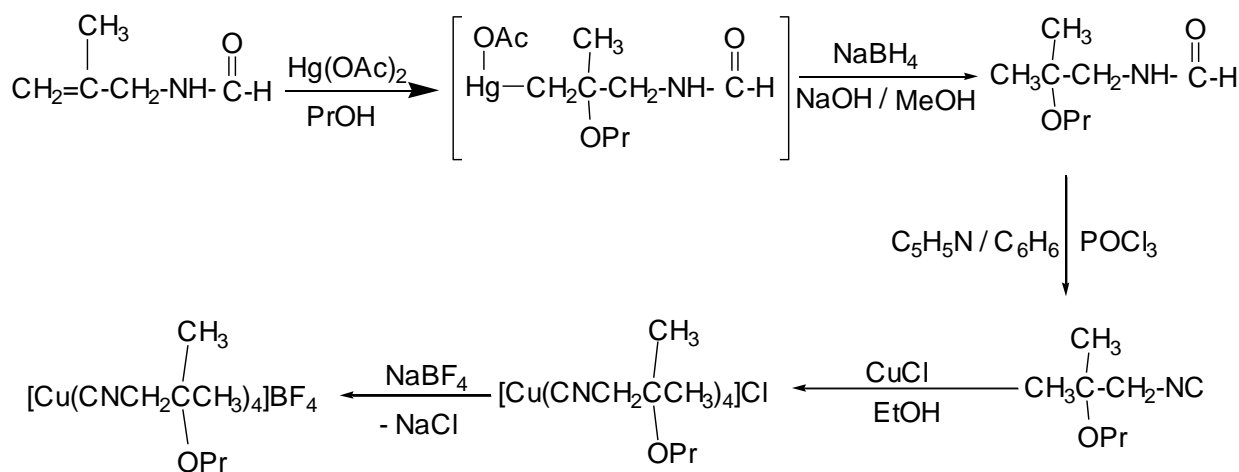


Fig. 1 – Schematic representation of MIBI, PIBI and their Cu(I) complexes.



Scheme 1 – Preparation of PIBI and its Cu(I) complex.

## RESULTS AND DISCUSSION

The title complex has a tendency to crystallize in the form of a very fine white powder. Since no single-crystal of good quality could be obtained, a crystal structure determination by powder X-ray diffraction study was attempted. The molecular structure of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  (Figure 2) shows a discrete monomeric unit  $[\text{Cu}(\text{PIBI})_4]^+$  with a tetrahedral Cu center coordinated to four PIBI ligands, each via its nitrite C atom with average Cu-C bond length and

mean C-Cu-C bond angle of  $1.963(7)$  Å and  $109.4(4)^\circ$  respectively. Both Cu-C bond distances and C-Cu-C angles of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  are very comparable to their corresponding ones in the structurally related  $[\text{Cu}(\text{MIBI})_4]\text{BF}_4$ .<sup>13</sup> The Cu-C-N bond angles are almost linear (the largest Cu-C-N angle is  $177.8(6)^\circ$  and the smallest angle is  $173.9(0)^\circ$ ) with average C-N bond distance of  $1.138(9)$  Å. Both of them lie in their normal ranges and they are comparable to their counterparts in  $[\text{Cu}(\text{MIBI})_4]\text{BF}_4$ .<sup>13</sup>

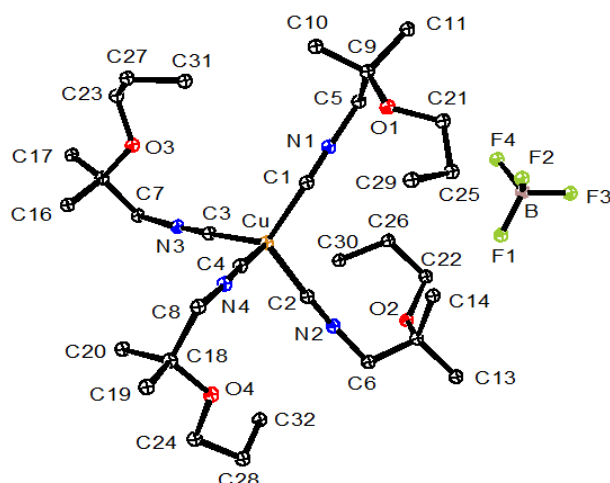


Fig. 2 – The molecular structure of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ , showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

The mentioned mean C-N distance (1.138 Å), which is rather close to the typical  $\text{C}\equiv\text{N}$  bond length (1.158 Å) in  $\text{CuCN}$ ,<sup>19</sup> as well as the linearity of Cu-C-N angles all suggest the C-N bond order of 3 in the complex  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ . The counter-

ion  $\text{BF}_4^-$  has an almost an ideal tetrahedral geometry with an average B-F bond distance of 1.350(4) Å, which is very similar to that of  $[\text{Cu}(\text{MIBI})_4]\text{BF}_4$ . Selected bond lengths and bond angles are depicted in Table 1.

Table 1

Selected bond lengths (Å) and angles for  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$

Cu–C1	1.955(5)	B–F2	1.350(2)
Cu–C2	1.975(9)	B–F3	1.352(7)
Cu–C3	1.960(1)	B–F4	1.349(9)
Cu–C4	1.963(3)	C1–Cu–C2	110.1(4)
C1–N1	1.128(9)	C1–Cu–C3	111.1(8)
C2–N2	1.127(5)	C1–Cu–C4	111.8(7)
C3–N3	1.144(4)	C2–Cu–C3	108.8(3)
C4–N4	1.155(1)	C2–Cu–C4	106.0(3)
N1–C5	1.479(0)	C3–Cu–C4	108.5(9)
N2–C6	1.457(7)	Cu–C1–N1	176.3(1)
N3–C7	1.451(3)	Cu–C2–N2	173.9(0)
N4–C8	1.423(5)	Cu–C3–N3	177.8(6)
B–F1	1.348(9)	Cu–C4–N4	175.1(4)

The crystal packing of the  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  complex is demonstrated in Fig. 3. It involves weak inter-molecular C—H $\cdots$ F contacts between the cations  $[\text{Cu}(\text{PIBI})_4]^+$  and  $\text{BF}_4^-$  anions, which link the components in a supramolecular three-dimensional network. For simplification, in the crystal packing of the studied complex, only those hydrogen bonds C—H $\cdots$ F (Table 2) lying within the sum of van der Waals radii for H and F atoms (2.67 Å) were considered as non-standard hydrogen bonds.<sup>20</sup> The crystal packing (Fig. 3) is achieved by C—H $\cdots$ F short contacts, where each individual  $[\text{BF}_4]^-$  anion is involved symmetrically by its four F atoms with three different surrounding  $[\text{Cu}(\text{PIBI})_4]^+$  cations to

form infinite supramolecular three-dimensional network. A particular  $[\text{Cu}(\text{PIBI})_4]^+$  cation is linked to three F centres of individual  $[\text{BF}_4]^-$  unit by three C—H $\cdots$ F short contacts. In the same manner, a different surrounding  $[\text{Cu}(\text{PIBI})_4]^+$  cation has contacts also with two F centers. The fourth F center has only short contact with a third adjacent  $[\text{Cu}(\text{PIBI})_4]^+$  cation. The mentioned non-standard hydrogen bondings are more likely effective in the stabilization of the crystal packing of the studied complex. The average C—H $\cdots$ F short distance within the crystal packing of the complex is in range (2.44–2.49 Å). Similar short C—H $\cdots$ F distances lying in range (2.20–2.60 Å) have been reported in

literature.<sup>21,22</sup> The C—H...F angles are larger than 120° (Table 2), the nonlinearity of C—H...F angles

in the crystal is probably due to other interactions in the packing effects.<sup>23</sup>

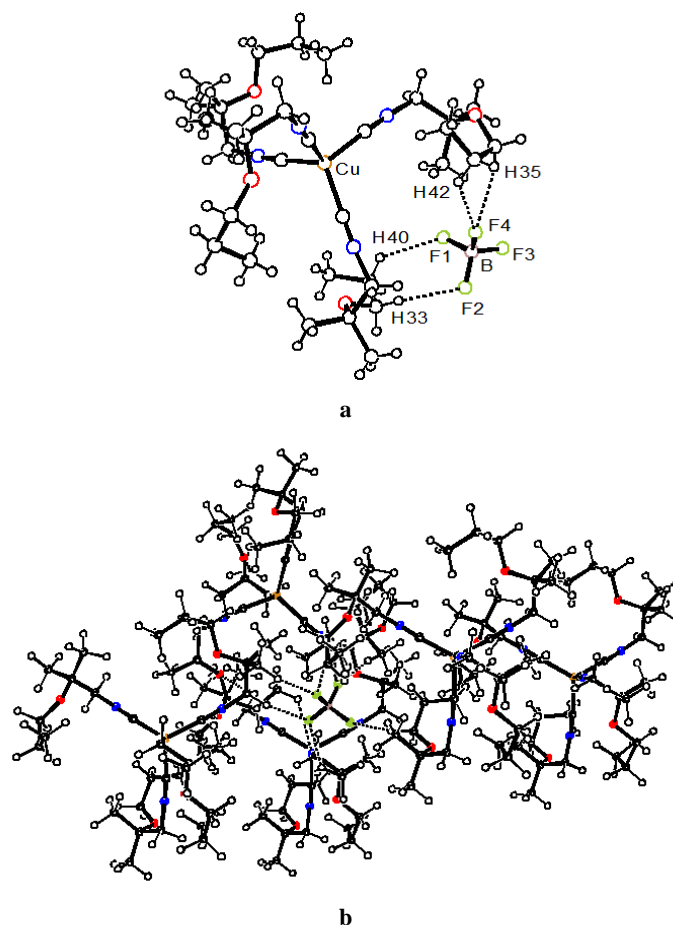


Fig. 3 – (a) The asymmetric unit of compound [Cu(PIBI)<sub>4</sub>]BF<sub>4</sub> showing the intra-molecular C—H...F short contacts. (b) The Portion of the packing diagram of [Cu(PIBI)<sub>4</sub>]BF<sub>4</sub>. Hydrogen bonds between ions are indicated by dashed lines.

Table 2

Hydrogen bond distances (Å) and bond angles (°) for [Cu(PIBI)<sub>4</sub>]BF<sub>4</sub>

D—H...A	d(D—H)	d(H...A)	d(D...A)	Angle(D—H...A)
C25 <sup>i</sup> —H40 <sup>i</sup> ...F1 <sup>i</sup>	0.951	2.470	3.180	131.33
C16 <sup>iii</sup> —H21 <sup>iii</sup> ...F2 <sup>i</sup>	0.907	2.441	3.051	124.76
C21 <sup>i</sup> —H33 <sup>i</sup> ...F2 <sup>i</sup>	0.954	2.479	3.313	145.97
C7 <sup>iii</sup> —H5 <sup>iii</sup> ...F2 <sup>i</sup>	0.952	2.771	3.476	131.53
C5 <sup>iii</sup> —H1 <sup>iii</sup> ...F3 <sup>i</sup>	0.952	2.471	3.392	162.81
C10 <sup>iii</sup> —H9 <sup>iii</sup> ...F3 <sup>i</sup>	0.952	2.735	3.601	151.46
C19 <sup>iv</sup> —H27 <sup>iv</sup> ...F3 <sup>i</sup>	0.953	2.455	3.154	130.11
C22 <sup>ii</sup> —H35 <sup>ii</sup> ...F4 <sup>ii</sup>	0.953	2.445	3.278	147.28
C26 <sup>ii</sup> —H42 <sup>ii</sup> ...F4 <sup>ii</sup>	0.953	2.890	3.498	122.74

**Symmetry code:** (i)  $x-1/2, y+1/2, z$ ; (ii)  $x, -y+2, z-1/2$ ; (iii)  $x+1/2, -y+3/2, z-1/2$ ; (iv)  $x-1/2, -y+3/2, z+1/2$ .

To the best of our knowledge there is no publication in literature concerning the crystal and molecular structure of [Cu(PIBI)<sub>4</sub>]BF<sub>4</sub>. A search of the Cambridge Structural Database (CSD, Version 5.42, update May 2022; Groom *et al.*, 2016) for the title complex gave no hits. However, a search on similar isonitrile Cu(I) complexes gave

the structurally related complexes: [Cu(MIBI)<sub>4</sub>] and [Cu(CNR)<sub>4</sub>]BF<sub>4</sub> (R = 2-(carbomethoxy-2-methylethyl)).<sup>13</sup> In both complexes, each Cu(I) center is bonded to four isonitrile carbon atoms adopting tetrahedral geometry, with the Cu—C distance ranging from 1.952 to 1.971 Å for [Cu(MIBI)<sub>4</sub>] and from 1.939 to 1.956 Å for

$[\text{Cu}(\text{CNR})_4]\text{BF}_4$  [where R = 2-(carbomethoxy)-2-methylethyl].<sup>13</sup>

### Hirshfield surface analysis

Hirshfield surface analysis was carried out to encapsulate and visualize the intermolecular interactions of supramolecular three-dimensional surface for the crystal. The program Crystal Explorer 17.5<sup>24</sup> was used to perform Hirshfield surface analysis. Molecular Hirshfield surfaces comprising of  $d_{\text{norm}}$  surface of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$

was generated using a standard (high) surface resolution and is illustrated in Fig. 4. The  $d_{\text{norm}}$  surface was mapped on over the range of  $-0.5806$  a.u. to  $1.9146$  a.u.. The  $d_{\text{norm}}$  mapping indicates strong C-H...F hydrogen bonding interaction as primary interaction seen as bright red spot. Nearly 77.7% of the total surface is captured by H...H short contacts resulting from the interaction of methyl and methylene hydrogens of  $[\text{Cu}(\text{PIBI})_4]^+$  and appear as scattered points in the plot.

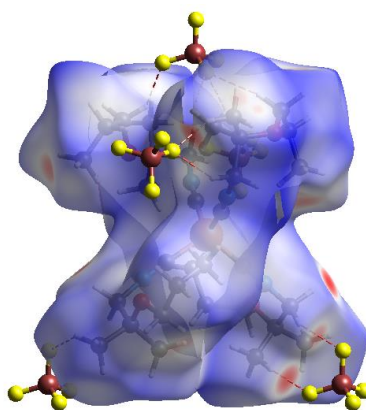


Fig 4 – Hirshfield surfaces mapped for  $d_{\text{norm}}$  surfaces of  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ .

A two-dimensional fingerprint plot contains information related to specific intermolecular interactions. The blue color refers to the frequency of occurrence of the  $(d_i, d_e)$  pair with the full fingerprint plot outlined in gray. Figure 5 shows the two-dimensional fingerprint plot for

the  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ , represented by the sum of the contacts contributing to the Hirshfield surface in normal mode. The most significant contribution to the Hirshfield surface comes from H...H contacts (77.7% Fig. 5a) and H...F (10.4% Fig 5b).

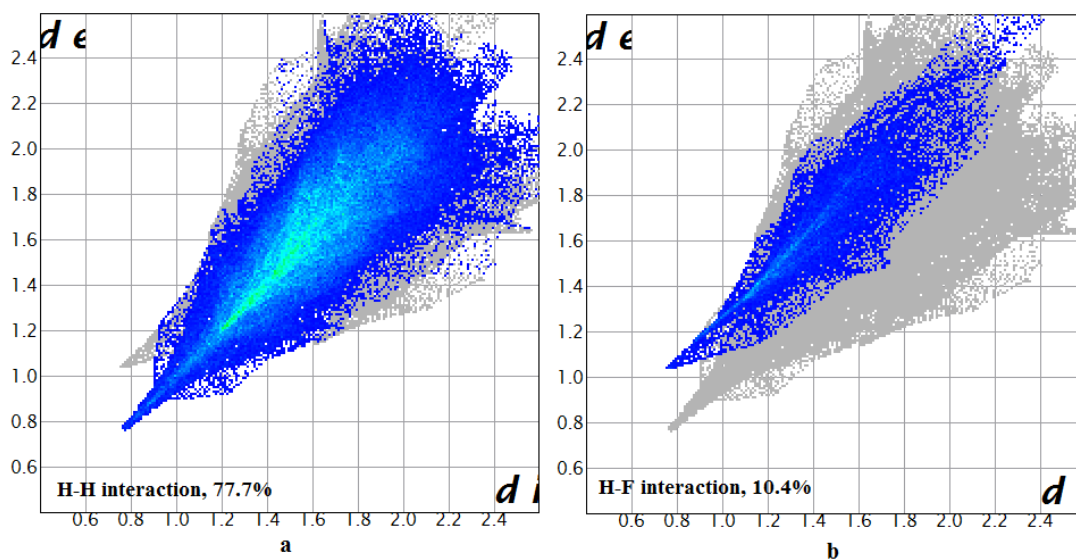


Fig. 5 – Relative contributions to the percentage of Hirshfield surface area for the various intermolecular contacts (a) H...H contacts and (b) H...F contacts, in the compound  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ .

## EXPERIMENTAL

### Materials

The title complex  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  was prepared and purified according to the previously reported method by us.<sup>18</sup> Powder X-ray diffraction was taken by *Stoe* Transmission diffractometer (*Stadi P*) (*Stoe & CIE GmbH*, Germany).

### Crystal structure determination for $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ from powder X-ray diffraction

The powder sample is ground in a mortar and loaded into two foils of Mylar. Then, it is fixed in a sample holder with a mask of internal diameter (7.0 mm). The pattern from  $3^\circ$  to  $90^\circ$  ( $2\theta$ ) is collected at room temperature and pressure in transmission geometry employing  $\text{Cu } K_{\alpha 1}$  radiation using (*STADI-P STOE*, Darmstadt, Germany) diffractometer, with  $\text{Cu } K_{\alpha}$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) and a germanium monochromator operated at 50 kV and 30 mA. Pattern indexing was performed with the program *DICVOL6.0*.<sup>25</sup> The first 20 lines of the powder pattern were completely indexed on the basis of a monoclinic cell. The figures of merit are sufficiently acceptable to support the obtained

indexing results [ $M(20) = 19.5$ ,  $F(20) = 49.6(0.0049, 82)$ ]. The *ab-initio* crystal structure was found by Simulated Annealing and the direct methods<sup>26</sup> as implemented in the *EXPO2014* program.<sup>27</sup> The found crystal is refined using the Rietveld method and Le Bail method for nonstructural parameter.<sup>28</sup> The found structure can be described as belonging to the monoclinic space group  $Cc$  with crystal parameters:  $a = 11.431 \text{ \AA}$ ;  $b = 25.736 \text{ \AA}$ ;  $c = 14.521 \text{ \AA}$ ;  $\alpha = \gamma = 90.0^\circ$ ;  $\beta = 103.661^\circ$ . Where the weighted profile R-factor and the un-weighted profile R-factor are  $R_{wp} = 2.896$  and  $R_p = 2.170$  respectively. The corresponding figures background-subtracted are  $R'_{wp} = 5.997$  and  $R'_p = 5.960$ . The Rietveld plots of the X-ray diffraction patterns are given in Fig. 6 for ( $2\theta$ ) from  $5.0^\circ$  to  $90^\circ$ . Someone notices that the observed and the calculated patterns are almost identical and there are no significant peaks beyond  $2\theta = 45^\circ$ .

The model found by *EXPO2014* was introduced into the program *GSAS-II*<sup>29</sup> for further Rietveld refinements as a starting point. The figure of merit  $M(20)$  is clearly improved and becomes 102. The final Rietveld plots of the X-ray diffraction patterns are given in Fig. 7. The final values of the crystallographic data and refinement goodness factors are shown in Table 3.

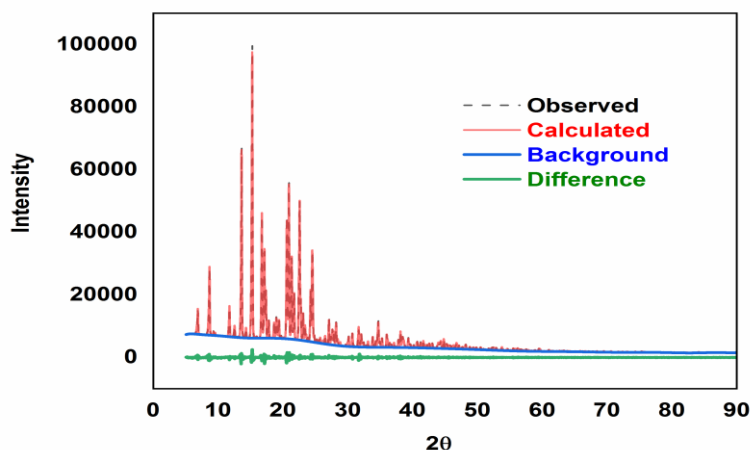


Fig. 6 – The final Rietveld plots for  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$  using *EXPO2014*. Observed data points are indicated by dashes (black), the best-fit profile (red line), background (blue line) and difference pattern (green line).

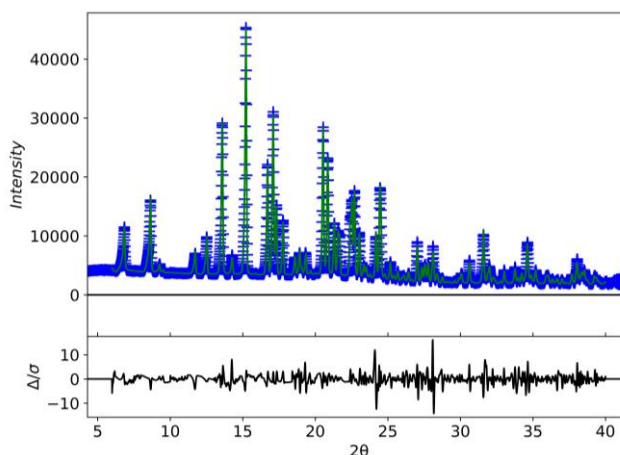


Fig. 7 – The final Rietveld pattern for  $[\text{Cu}(\text{PIBI})_4]\text{BF}_4$ . The (blue +) is the observed values and (green -) are the fitted ones. Black line is the difference between the observed and the fitted values.

Table 3  
Experimental details

Chemical formula	C <sub>32</sub> H <sub>60</sub> BCuF <sub>4</sub> N <sub>4</sub> O <sub>4</sub>
<i>M<sub>r</sub></i>	715.2
Crystal system, space group	Monoclinic, <i>Cc</i>
Temperature (K)	300
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4710 (3), 25.8335 (3), 14.5531 (4)
β (°)	103.6461 (11)
<i>V</i> (Å <sup>3</sup> )	4190.86 (5)
<i>Z</i>	4
Radiation type	Kα <sub>1,2</sub> , λ = 1.54051, 1.54433 Å
μ (mm <sup>-1</sup> )	0.75
Specimen shape, size (mm)	Cylinder, 8 × 7
<b>Data collection</b>	
Diffractometer	Stoe
Specimen mounting	Powder loaded between two Mylar foils
Data collection mode	Transmission
Scan method	Step
2θ values (°)	2θ <sub>min</sub> = 2.97 2θ <sub>max</sub> = 89.96 2θ <sub>step</sub> = 0.01
<b>Refinement</b>	
<i>R</i> factors and goodness of fit	<i>R<sub>p</sub></i> = 0.021, <i>R<sub>wp</sub></i> = 0.031, <i>R<sub>exp</sub></i> = 0.015, <i>R</i> ( <i>F</i> <sup>2</sup> ) = 0.00000, χ <sup>2</sup> = 4.356
No. of parameters	5
H-atom treatment	All H-atom parameters refined

## CONCLUSION

The molecular and crystal structure of the previously reported [Cu(PIBI)<sub>4</sub>]BF<sub>4</sub> was confirmed by powder X-ray diffraction study. The molecular structure showed that this complex has a tetrahedral coordination geometry with four PIBI ligands bound to the same Cu(I) center. The counter-ion BF<sub>4</sub><sup>-</sup> has almost an ideal tetrahedral geometry. The crystal packing is achieved by C—H⋯F short contacts to form infinite supramolecular three-dimensional network.

*Supplementary information.* CCDC 2270318 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/)

[conts/retrieving.html](#) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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