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Contributed Paper

Structural Analysis of Powder Complex of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$)

Cahyorini Kusumawardani, Fitra Kainastiti and Kristian Handoyo Sugiyarto*

Department of Chemistry Education, Faculty of Mathematics and Natural Science,

Yogyakarta State University, Kampus Karangmalang, Jl. Colombo No. 1, Yogyakarta, 55281, Indonesia.

* Author for correspondence; e-mail: sugiyarto@uny.ac.id

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ABSTRACT

The powder complex of tris-bipyridinecopper(II) trifluoromethanesulfonate quasi to mono hydrate has been synthesized by the interaction of the corresponding nitrate salt and slightly excess of bipyridine in aqueous solution with drops of ethanol, whereupon the precipitate was produced by addition of an excess of saturated potassium triflate solution on reducing the solvent. AAS measurement showed the content of metal to be 7.54 % corresponding to the theoretical value of 7.56 % in $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$). The analysis of conductance producing the charge ratio of cation by anion to be 2: 1, clearly confirms the formula. The magnetic moment, μ_{eff} of this complex which was to be 1.73-1.83 B.M, indicates that the complex is paramagnetic corresponding to an unpaired electron. UV-Vis spectrum of the complex reveals the only one absorption observed at about 681.50 nm (14673.51 cm^{-1}), being associated with the spin allowed transition, ${}^2E_g \rightarrow {}^2T_{2g}$. The extinction coefficient of $57.8 \text{ Lmol}^{-1}\text{cm}^{-1}$ indicates the adoption of the octahedral environment in this complex. The infrared spectrum shows absorptions of ligand group which is influenced by the metal-ligand interaction in this complex. The powder XRD analysis of this complex was refined by Le Bail method of Rietica program and found to be fit as monoclinic crystal system with space group of $C2/c$, and cell parameters of $a = 13.662 \text{ \AA}$, $b = 23.040 \text{ \AA}$, $c = 29.268 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 100.15^\circ$, $\gamma = 90^\circ$, $V = 9069.05 \text{ \AA}^3$, $R_p = 5.5$, and $R_{wp} = 9.94$ and $R_{exp} = 2.68$ leading to χ^2 (GOF) value of 13.72. The goodness of the fitting might be also reflected by the derived Bragg R-Factor of 0.02.

Keywords: Rietica, Le Bail, bipy, triflate, copper(II), powder XRD

1. INTRODUCTION

The synthesis and characterization of complexes containing copper(II) along with other metal divalent such as Ni(II), Co(II), Fe(II), and Ru(II) with 2,2'-bipyridine (bipy) as ligand have been reported a long time ago.

The counter ions in these complexes were Cl^- , I^- , and SO_4^{2-} [1]. In the case of copper(II) the chloride salt has been reported to form six-coordinate of tris-bipyridinecopper(II). However, for the iodide salt, the five-

coordination of iodidobis-pyridinecopper(II) cation was produced. It is true that four- and five-coordinate copper(II) complexes are also very common with any bidentate ligand. Thus, another five- and four-coordinate copper(II) complexes of 2,2'-bipyridine have also been observed [2,3,4].

It has been also long known that the trifluoromethanesulfonate (known as triflate) salts were already recognized as highly ionic, it is because the corresponding acid might be considered as super-acid which is much stronger than sulphuric acid with Hammett acidity to be -12 [5,6]. In many cases triflate ionic liquids are hydrolytically stable and they are the preferred reaction media in comparison to ionic liquids with the hydrolytically unstable PF_6^- or BF_4^- anions [7], and known as a weakly coordinating anion [8]. In this sense, the triflate anion seems to act as a counter anion rather than coordinate to the metal atom. Therefore the copper(II) complex containing 2,2'-bipyridine with triflate anion should result in highly ionic complexes and then the bipyridine ligand might exert to form the six-coordinate complex, and this is the main purpose of this work. If it is so, a distorted octahedral structure of $[\text{Cu}(\text{bipy})_3]^{2+}$ cation might be produced due to Jahn-Teller effect and perhaps this may be identified by unsymmetric band of its electronic spectral property.

2. MATERIALS AND METHODS

2.1 Materials

The main chemicals, copper nitrate ($\text{Cu}(\text{NO}_3)_2$), bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$), potassium triflate (KCF_3SO_3), ammonium chloride (NH_4Cl), calcium chloride (CaCl_2), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), and aluminium chloride (AlCl_3) were purchased from Sigma-Aldrich. All the reagents were used without further purification.

2.2 Preparation of Tris-bipyridinecopper(II)

About 10 mL of an aqueous solution of 0.1 mmol $\text{Cu}(\text{NO}_3)_2$ and 5 mL solution of 0.32 mmol bipyridine in water/ethanol were mixed. The mixture was well stirred and heated to obtain a homogeneous solution. To this solution, an excess of saturated aqueous solution of KCF_3SO_3 (0.4 mmol in 5 mL) was added. The mixture was concentrated on heating, and the obtained powder on cooling was then filtered, rinsed with a minimum of cold water, and then dried in aeration.

2.3 Physical Measurements

Magnetism. The magnetic data for the solid sample were obtained at room temperature only by using *Magnetic Susceptibility Balance* (MSB) of Auto Sherwood Scientific 10169 model, calibrated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The molar magnetic susceptibility data were then corrected for diamagnetism calculated using Pascal's constant [9]. The corresponding effective magnetic moment (μ_{eff}) was then calculated from the corrected molar magnetic susceptibility following the general formula, $\mu_{\text{eff}} = 2.828 \sqrt{\chi_M T}$ B.M.

Electronic and Infrared Spectra. The electronic spectrum of the solid sample was recorded on Pharmaspec UV 1700 spectrophotometer. The powders were spread on a 2x2 cm particular thin glass adhered with ethanol. The fitting was then placed in the cell holder and the spectrum was recorded at 400-1000 nm. The infrared spectrum of the powdered sample which was pressed on the cell was recorded on an infrared spectrophotometer FTIR Shimadzu Prestige 21 at 500-4000 cm^{-1} .

Metal Content and Ionic Property. The metal content in the sample was calculated based on the data recorded using an Atomic

Absorption Spectrophotometer of Shimadzu AA-6650 model. While the ionic property was estimated by recording the electrical (equivalent) conductance by using a conductometer calibrated with an aqueous solution of 1 M potassium chloride at 25°. The obtained data of sample was compared to those of known ionic solutions, NH_4Cl , CaCl_2 , $\text{Ni}(\text{NO}_3)_2$, and AlCl_3 , which were also recorded with the same conductometer.

Powder X-Ray Diffraction. The diffractogram of the complex was recorded by using a Rigaku Miniflex Benchtop Diffractometer, $\text{CuK}\alpha$, $\lambda=1.5406 \text{ \AA}$. The powdered sample was spread on the glass plate and then was placed on the cell holder. The reflection data were recorded in scan mode at 2-90 (degree of 2θ) with an interval of 0.02 and rate of 10. The resulting diffractogram was then analysed by Rietica program of Le Bail method (5-90 degree of

2θ) being usually applied to metal oxides [10,11,12], which was run within 30 cycles. (Note that selected data of refinement is available as material supplement).

3. RESULTS AND DISCUSSIONS

3.1 Chemical Formula of the Complex

Direct interactions of the ligand, bipyridine, and the copper(II) salt in solution produced the blue cationic complex which could be precipitated on the addition of triflate salt. The electrical equivalent conductance of this complex was recorded with respect to the known ionic simple compounds in aqueous solution, and the result is shown in Table 1. It suggests that the corresponding value is in the range of ionic compounds with three ions per molecule, and thus the possible empirical formula of $\text{Cu}(\text{bipy})_n(\text{CF}_3\text{SO}_3)_{3/2}(\text{H}_2\text{O})_x$ is then proposed for this powdered complex.

Table 1. Electrical equivalent conductance of the complex and some known salts.

Compounds	Equivalent conductance (Λc) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Ratio of cation/anion	Number of ions
NH_4Cl	78.05	1 : 1	2
CaCl_2	127.85	1 : 2	3
$\text{Ni}(\text{NO}_3)_2$	124.21	1 : 2	3
AlCl_3	171.70	1 : 3	4
$\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_{3/2}(\text{H}_2\text{O})_x$	113.30	1 : 2	3

The coordination number of the empirical formula, n , and the number of hydrates, x , were then estimated on the basis of metal content obtained by atomic absorption spectral data as shown in Table 2. This suggests that the chemical formula of the complex would be *tris-*

bipyridinecopper(II), $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$, where x probably 0, 0.5, 1, as expected from the stoichiometric preparation. The conductivity data of this complex confirms the highly ionic property of the triflate salts [5, 8].

Table 2. The proposed formula of complex following the metal content.

Compound	Metal content	
	Theoretic calculation (%)	AAS result (%)
$\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2$	7.65	
$\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{H}_2\text{O}$	7.57	7.54
$\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot 1\text{H}_2\text{O}$	7.49	

3.2 Magnetic Moment

On the basis of the formula as shown in Table 2, the magnetic susceptibility data obtained on the measurement (Table 3) were then calculated to the magnetic moment and the result of the three separated samples, in fact, to be normal paramagnet, 1.66-1.82 B.M., being spin-only value of one unpaired electron in the d^9 electrons of Cu(II), as also observed in the corresponding perchlorate [13]. Thus, no orbital contribution to the magnetism was considered in this instance.

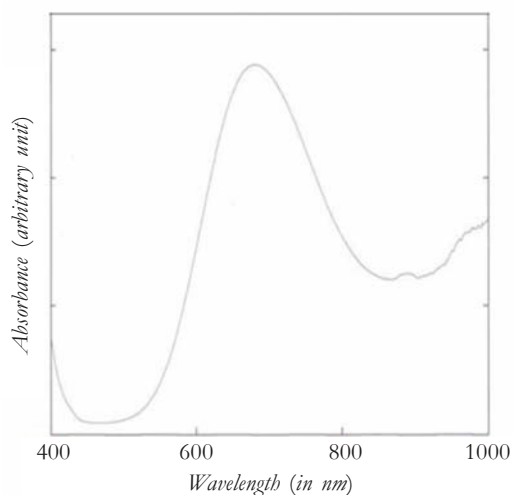
Table 3. Magnetic data of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0, 0.5, 1$) at room temperature.

Sample	$\chi_g \times 10^{-6}$ (cgs)	Moment Magnetik (BM)
1	0.965	1.66-1.74
2	1.080	1.71-1.80
3	1.105	1.73-1.82

3.3 Electronic Spectrum

The electronic spectrum of the powder complex recorded at 400-1000 nm as shown in Figure 1, reveals clearly a well resolved main absorption band concentrated at about 681.5 nm (14673 cm^{-1}) which is attributed to the spin allowed transition of ${}^2E_g \rightarrow {}^2T_{2g}$, which is quite the same (680 nm) as observed in the corresponding perchlorate [13] and hexafluorophosphat [14], and close to other anions (690 nm) [15,16], reflecting the ligand field strength of bipyridine surrounding Cu(II) metal ion. The relatively slight unsymmetric-

pattern of the absorption band suggests a slight distortion as confirmed by the distorted octahedral configuration as reported from the single crystal structure of the perchlorate [13,17].

**Figure 1.** Electronic spectrum of powder $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0, 0.5, 1$).

3.4 Infrared Spectrum

The infrared spectra of various metal complexes with bipy have been reported [18,19,20,21,22]. In a comparison of the infrared spectrum of bipy with those of its complexes, Shinha [18] observed that considerably shifted absorption bands of the functional group of bipy have occurred due to chelation. With rare-earth metals, the absorptions at region $1470\text{-}1500 \text{ cm}^{-1}$ (vs), 1320 cm^{-1} (s), and $700\text{-}800 \text{ cm}^{-1}$ were observed. The ring modes of bipy in divalent metals (Mn, Co, Ni) complexes [21], were

observed at around 1600 and 1570 cm^{-1} ($\mu_{\text{C-C}}$ and $\mu_{\text{C-N}}$), 1020 cm^{-1} (bipy 'breathing'), and 715-770 (C-H out of plane bend). In this work as shown in Figure 2, the infrared spectrum of this complex recorded at 500-4000 cm^{-1} reveals the typical strong ring modes of bipy at about 1604, 1570, 1004, and 770 cm^{-1} , being quite similar to those observed in Cu(II)-bipy complex [22] and also other divalent metals [21] and therefore it is due to chelation. The mode observed at

1625-1635 cm^{-1} in the spectrum might be due to molecule of H_2O as proposed by Shinha [18] when comparing to other anhydrous complexes. Moreover, broad absorption at about 3500 cm^{-1} should be clearly due to stretching mode of -OH of H_2O . If it is so, the absence of water molecule ($x = 0$) in the complex should be possible, and therefore, the formula of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) seems more reasonable.

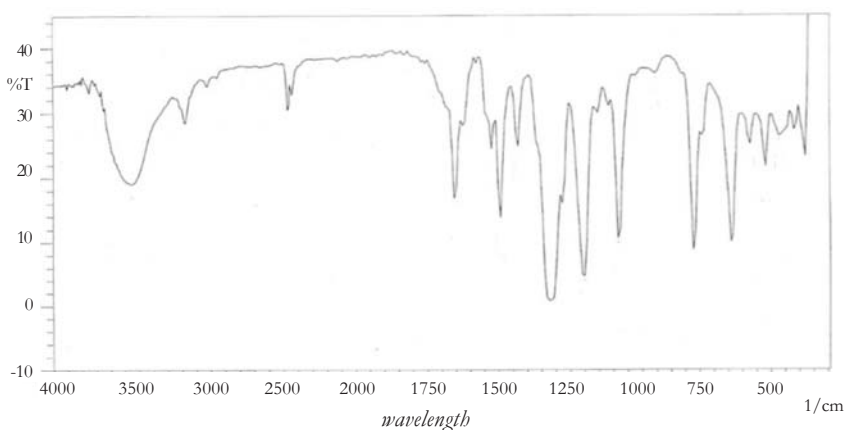


Figure 2. Infrared spectrum of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$).

In the case of triflate ion, the infrared of some metallic triflate salts is used as a comparison [8]. Thus, as shown in Figure 2, the corresponding infrared spectrum can be assigned readily. The modes of vibrations observed at 1265 and 1149 cm^{-1} are to be SO_3 and CF_3 asymmetric stretching modes, respectively, while those at 1030 and 1225 cm^{-1} are SO_3 and CF_3 symmetric stretching modes, respectively. The bands at 771 and 640 cm^{-1} are likely deformation symmetry of CF_3 and SO_3 , respectively, and the bands at 571 and 517 cm^{-1} are deformation asymmetry of CF_3 and of SO_3 , respectively. Therefore, the infrared data strongly suggest that the complex sample should contain the chelation of bipy to copper(II) and free triflate anion.

3.5 The Powder X-ray Diffraction and Structural Analysis

The single crystal of cation $[\text{Cu}(\text{bipy})_3]^{2+}$ with particular anions has been reported. For the chromate, $[\text{Cu}(\text{bipy})_3]\text{CrO}_4 \cdot 7.5\text{H}_2\text{O}$, the crystal adopts monoclinic symmetry of the space group, $\text{C}2/c$ [15]. While for the tetraphenylborate, $[\text{Cu}(\text{bipy})_3](\text{BPh}_4)_2$ it is also monoclinic symmetry but of space group of $\text{P}21/c$ [16]. For the perchlorate, however, two single crystals have been produced separately [13,17], and they have been refined to have significantly different cell parameters (Table 4). Surprisingly both are the same in triclinic symmetry of the same group space, $\text{P}1$. All of the tris-bipyridinecopper(II) cations show distorted octahedral geometry. While the different cell parameters in both

perchlorates might be due to different method in crystal growth, the more surprising nature in tris-bipyridinecopper(II) perchlorate still went on. Liu *et al* [23] observed the single crystal tris-bipyridinecopper(II) perchlorate to be distorted square-pyramidal geometry and thus only five nitrogen atoms of the tris-bipy bind to copper(II) ion. These might reflect that copper(II) could be stable in both five- and six- coordinated configurations.

From those facts, the powder X-ray diffraction of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_{3/2}(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) was then recorded, and the diffractogram together with its refinement is shown in Figure 3. The black signs (+) represent the observed experimental data, the red full line is the refinement according to Rietica-Le Bail program (at 5-55 degree of 2 theta) for the expected model of monoclinic symmetry of space group $C2/c$

which are the blue bar-lines, and the green curve indicates the different between the observed diffractogram and the analysis result.

As shown in Figure 3, it is clear that the red full line does almost pass through the black observed data, and it is demonstrated by the almost flat green curve, indicating that the corresponding analysis is almost perfect with derived Bragg R-Factor of 0.02, R_p , R_{wp} , and R_{exp} values of 5.5, 9.94, and 2.68, respectively, leading to reasonably χ^2 value of 13.72. Detailed results of cell parameters of the crystal structure are presented in Table 4 together with known single crystal data of the same cation, of the chromate [15], tetraphenylborate [16], and of the perchlorate complexes [13,17,23]. Thus in this work, the complex might be considered to adopt monoclinic symmetry of the same space group, $C2/c$.

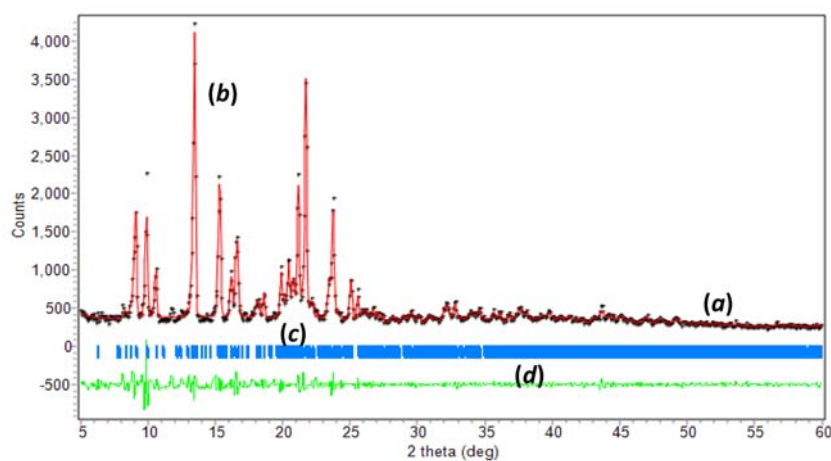


Figure 3. Diffractogram of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_{3/2}(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) (black sign +, **a**), and of refined triclinic space group of $C2/c$ model (red full line, **b**) with its position of 2 theta (blue bars, **c**), and the difference between the black observed and the red refined model (green, **d**).

Table 4. Detailed cell parameters of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) due to *Rietica* program of *Le Bail* method and of other single crystals.

[Cu(bipy) ₃](X)	X=	X=	X=	X=	X=	X=
	$\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) (This work)	$\text{CrO}_4 \cdot 7.5\text{H}_2\text{O}$ [15]	$(\text{BPh}_4)_2$ [16]	$(\text{ClO}_4)_2$ [23]	$(\text{ClO}_4)_2$ [17]	$(\text{ClO}_4)_2$ [13]
Symmetry	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space Grup	C2/ c	C2/ c	P21/c	PI	PI	PI
a (Å)	13.662	13.681	12.5437	7.904	12.673	7.927
b (Å)	23.040	22.921	14.4955	11.092	18.440	11.0236
c (Å)	29.268	23.321	35.1285	18.471	7.937	18.4768
V (Å ³)	9069.0	7081	6237.6	1569.0	n.a	1572.9
α (°)	90	90	90	79.69	90.37	79.648
β (°)	100.15	104.46	102.43	89.88	120.56	89.79
γ (°)	90	90	90	82.15	98.80	82.110
R _p	5.50					
R _{wp}	9.94					
R _{exp}	2.68					
Z	4	4	4	2	2	2
R _{Bragg}	0.02					
GOF (χ ²)	13.72	1.277	n.a	n.a	n.a	1.8

It might be noted that the application of Le Bail method of Rietica program has not been performed to many powdered complexes. The first fitting might come from Zhu, Wu, and Le Bail himself in 1999 [24] who demonstrated the best fitting for powdered of cobalt complex containing monodentate of amine. It resulted in very low R factors, being 0.053 for R_{Bragg} , 0.1 for R_p , 0.119 for R_{wp} and 0.04 for R_{exp} leading to 8.85 for χ^2 . The next application was performed on powdered ruthenium complexes with a mixture of ligands containing bipy in 2008 [25]. The reasonably good fittings resulted in derived Bragg R-factors of 0.0048-0.0128 and χ^2 of 1.9-9.75. Finally, the application of Le Bail method was performed on oxalate complexes in 2009 [26]. It seems, however, likely more appropriate to bimetal-oxides rather than general coordination compounds. The refined

plot of powder diffractograms seem quite good, nevertheless, the resulted refinement showed in fact much high values of R factors, being 16.4-17.9 for R_p , 13.3-13.58 for R_{wp} and high values of 279.36-290 for $(R_{\text{wp}}/R_{\text{exp}})^2$ or χ^2 . Quite recently, Sugiyarto *et al* [27] reported the powder XRD of $[\text{Mn}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot 6.5\text{H}_2\text{O}$. The fitting was quite good with the R values of 0.16 (R_{Bragg}), 3.67 (R_p), 7.34 (R_{wp}), and 3.61 (R_{exp}), leading to χ^2 value of 4.13. "How good is good enough" of the fittings is in fact still not so easy to conclude as discussed by Toby [28] concerning how low of R factors.

4. CONCLUSIONS

The powder of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_x$ ($x = 0.5, 1$) has been synthesized. The magnetic moment was found to be 1.7-1.8 B.M., being normal paramagnet for an unpaired electron of Cu(II). The

electronic spectral property of the powder complex reveals the main absorption band concentrated at about 681.5 nm (14673 cm^{-1}), which is attributed to the spin allowed transition, ${}^2E_g \rightarrow {}^2T_{2g}$. The infrared spectrum of the complex recorded at the range $500\text{-}4000\text{ cm}^{-1}$ shows the typical vibration bands of function groups of 2,2'-bipyridine and the corresponding triflate anion. The corresponding Powder X-Ray Diffraction analysed by *Rietica* program of *Le Bail* method suggests that the complex adopts monoclinic symmetry of space group *C2/c* with the derived Bragg R-factor, 0.02 and χ^2 value of 13.72.

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