

Synthesis and Structural Analysis of Powder Complex of Tris(bipyridine)cobalt(II) Trifluoromethanesulfonate Octahydrate

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ABSTRACT

The powder complex of tris(bipyridine)cobalt(II) trifluoromethanesulfonate octahydrate has been synthesized by direct interaction of the corresponding aqueous solutions (and drops of ethanol) of cobalt(II) nitrate, bipyridine, and potassium triflate. The yellow-orange powder produced was filtered off and allowed to dry on an aeration for characterization. AAS measurement showed the content of metal to be 6.06%, corresponding to the theoretical value of 6.06% in $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$. The analysis of conductance producing the charge ratio of cation to anion to be 2:1, confirms the formula. The magnetic moment, μ_{eff} , of this complex which was to be 4.5-4.9 BM, indicates that the complex is paramagnetic corresponding to the three unpaired electrons with a significantly orbital contribution. UV-Vis spectrum of the complex reveals the first band observed at about 11100 cm^{-1} , which is associated with the spin-allowed transition, ${}^4T_{1g} \rightarrow {}^4T_{2g}$. A distinct shoulder at only about 16100 cm^{-1} should be associated with the spin-forbidden transition of ${}^4T_{1g} \rightarrow {}^2T_{2g}, {}^2T_{2g} (\text{G})$. The expected second and third bands which are associated with spin-allowed transitions of ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}$ at higher energy were not well resolved. The infrared spectrum shows absorptions of the functional group of ligand which is influenced by the metal-ligand interaction in this complex. The powder XRD of this complex was refined using Le Bail method of Rietica program and found to be fit as monoclinic symmetry with a space group of C2/c.

Keywords: Rietica; Le Bail; bipy; trifluoromethanesulfonate; cobalt(II)

ABSTRAK

Serbuk kompleks tris(bipiridine)kobalt(II) trifluorometanasulfonat telah berhasil disintesis melalui interaksi langsung larutan air dengan beberapa tetes etanol dari kobalt(II) nitrat, bipiridin, dan kalium triflat. Serbuk kuning-oranye yang terbentuk disaring dan dikeringkan untuk keperluan karakterisasi. Pengukuran AAS yang menunjukkan kandungan logam 6,06%, sesuai dengan nilai teoretis 6,06% pada $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$. Analisis daya hantar listrik ekuivalen menghasilkan rasio muatan kation/anion 2:1, menegaskan formula tersebut. Momen magnetik, μ_{eff} , sebesar 4.5-4.9 BM, menunjukkan kompleks bersifat paramagnetik yang sesuai dengan tiga elektron nir-pasangan dengan kontribusi orbital yang kuat. Spektrum UV-Vis kompleks mengungkap pita pertama pada 11100 cm^{-1} , yang diasosiasikan dengan transisi spin-terijin, ${}^4T_{1g} \rightarrow {}^4T_{2g}$. Suatu pundak yang sangat jelas pada 16100 cm^{-1} menunjuk pada transisi spin-terlarang, ${}^4T_{1g} \rightarrow {}^2T_{2g}, {}^2T_{2g} (\text{G})$. Pita kedua dan ketiga yang diharapkan menunjuk pada transisi spin-terijin ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ dan ${}^4T_{1g} \rightarrow {}^4A_{2g}$ pada energi yang lebih tinggi tidak muncul secara jelas. Spektrum infra merah menunjukkan serapan gugus-fungsi khas bagi ligan yang dipengaruhi oleh interaksi logam-ligan. Difraksi sinar-X serbuk kompleks ini yang dianalisis menurut metode Le Bail dalam program Rietica menghasilkan simetri kristal monoklin dengan grup ruang C2/c.

Kata Kunci: Rietica; Le Bail; bipy; trifluorometanasulfonat; kobalt(II)

INTRODUCTION

The chemistry of Co(II) complexes with bidentate ligands such as ethylenediamine (*en*) [1], phenanthroline (*phen*) [2] and bipyridine (*bipy*) [3] have been well known. In particular, the crystal structure of $[\text{Co}(\text{bipy})_3](\text{ClO}_4)_2$ has also been determined [4]. Quite recently the application of cobalt redox shuttle, Co(II) and Co(III) complexes of *tris-*

bipy, to make a dye-sensitized solar cells (DSSC) electrolyte has also been developed [5].

The salts of trifluoromethanesulfonate (triflate) have also been recognized to be highly ionic. The corresponding acid might be classified as super-acid, being much stronger than sulphuric acid with Hammett acidity to be -12 [6]. In many cases triflate, the ion is more hydrolytically stable than PF_6^- or BF_4^- anions and is also known as a weakly coordinating anion [7]. Thus,

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the triflate anion seems to act as a counter anion rather than coordinate to the metal atom. Therefore the cobalt(II) complex containing 2,2'-bipyridine with triflate anion should result in highly ionic complex and then the bipyridine ligand might exert to form the six-coordinate complex, and this is the main purpose of this work. Since it is not so simple to prepare and then solve a single crystal of the corresponding complex, collecting powder XRD of this complex and then refining this using Le Bail method of Rietica program is another alternative at least to identify the cell parameters.

EXPERIMENTAL SECTION

Materials

The main chemicals, cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2$), 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.

Preparation of the Complex

No special instrument was employed in the sample preparation of the complex. Thus, the complex was prepared according to the followings. The mixture containing 0.1 mmol $\text{Co}(\text{NO}_3)_2$ and 0.32 mmol bipyridine in about 15 mL aqueous solution with drops of ethanol was well stirred and warmed till solution become clear. An excess of a saturated aqueous solution of KCF_3SO_3 (0.4 mmol in 5 mL) was added to this solution. The mixture was concentrated on heating, whereupon the yellow-orange solid was deposited on scratching while cooling. It was then filtered, rinsed with a minimum of cold water, and then dried in exposure. Three samples of the complex were separately prepared in this work.

Physical Measurements

Magnetism

The magnetic susceptibility for powder samples was 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. The corresponding effective magnetic moment (μ_{eff}) was then calculated from the corrected molar magnetic susceptibility following the general formula, $\mu_{\text{eff}} = 2.828 \sqrt{\chi_{\text{M}} \cdot T}$ BM.

Electronic and infrared spectra

The electronic spectrum of the solid sample was recorded on Pharmaspec UV 1700 spectrophotometer. The powders were spread on a 2 x 2 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 estimated 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 1.0 M potassium chloride at 25 °C. The obtained data of the 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 powder complex was recorded by using a Rigaku Miniflex Benchtop Diffractometer, $\text{CuK}\alpha$, and $\lambda = 1.5406 \text{ \AA}$. 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 analyzed by Le Bail method of Rietica program (5–50 degree of 2θ) being usually applied to metal oxides [e.g., 8–10], which was run within 30 cycles.

RESULT AND DISCUSSION

Chemical Formula of the Complex

The interactions of the ligand, bipyridine, and the cobalt(II) salt in solution produced the yellow-orange cationic complex which could be precipitated on the addition of triflate salt in excess (Yield: 88–90% w/w). The equivalent electrical conductance of this complex was recorded besides the well-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 $[\text{Co}(\text{bipy})_n](\text{CF}_3\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$ is then proposed for this powder complex.

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

Compounds	Equivalent conductance (Λ c) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Ratio of cation/anion	Number of ions per molecule
NH_4Cl	78.05	1 : 1	2
CaCl_2	127.84	1 : 2	3
$\text{Ni}(\text{NO}_3)_2$	124.21	1 : 2	3
AlCl_3	161.07	1 : 3	4
$\text{Co}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$	121.65	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 only, obtained by atomic absorption spectral data as shown in Table 2. This suggests that the chemical formula of the complex would be *tris*(bipyridine)cobalt(II) octahydrate, $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$, as expected from the stoichiometric preparation. The conductivity data of this complex confirms the highly ionic property of the triflate complex [6-7].

Magnetic Moment

On the basis of the formula 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 are 4.5–4.9 BM. In fact, it is to be normal paramagnet, corresponding to three unpaired electrons of high spin Co(II). These values are significantly higher than that of spin only value (3.87 BM) being due to highly orbital contribution to the magnetism and this reflects the triply ground term of $^4T_{1g}$ in an octahedral configuration which is commonly observed in high spin Co(II) complexes. These values are not significantly different from that observed by Lee, Griswold, and Kleinberg, that was 4.9–5.1 BM [11].

Electronic Spectrum

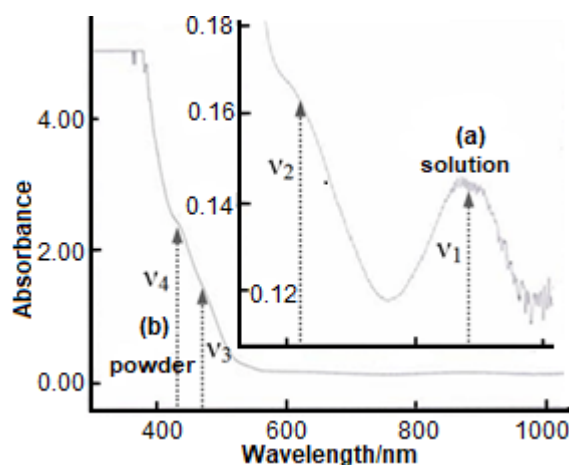
The electronic spectrum of a single crystal of $[\text{Co}(\text{bipy})_3](\text{CrO}_4)_{0.5}(\text{NO}_3) \cdot 7\text{H}_2\text{O}$ has been analyzed by Wojsiechowska et al. [12], resulting in Dq of 1196 cm^{-1} and B of 706 cm^{-1} . Taking the value of Dq/B , which is about 1.69, into the Tanabe-Sugano diagram, it can be deduced that the increasing energy of quartet states are to be $^4T_{1g}(\text{F})$, $^4T_{2g}(\text{F})$, $^4T_{1g}(\text{P})$, and $^4A_{2g}(\text{F})$, respectively. In this work, the electronic spectra of the solution and powder $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$ were recorded at 400–1000 nm as shown in Fig. 1. In Fig. 1(a) (inset), it reveals clearly a well resolved main first absorption band concentrated at about 900 nm (11110 cm^{-1}) with the extinction coefficient of $14.5\text{ L mol}^{-1}\text{ cm}^{-1}$, indicating an octahedral configuration. This is in good agreement with that observed ($11100\text{--}11250\text{ cm}^{-1}$) by Palmer and Piper [3]. Thus, no doubt it is then attributed to the spin-allowed

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

Compound	Metal content	
	Theoretic calculation (%)	AAS result (%)
$\text{Co}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$	6.18	
$\text{Co}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$	6.06	6.06

Table 3. Magnetic data of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$ at room temperature

Sample	$\chi_M' \times 10^{-6}$ (cgs)	Magnetic Moment (BM)
1	10185	4.927
2	9082	4.652
3	8561	4.517

**Fig 1.** Electronic spectrum of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$

transition of v_1 : $^4T_{1g} \rightarrow ^4T_{2g}$. The surprisingly strong shoulder centered at about 620 nm (16130 cm^{-1}) should be associated with the spin-forbidden transition of v_2 : $^4T_{1g} \rightarrow ^2T_{1g}, ^2T_{2g}$ (G), which is again in agreement with that proposed by Palmer and Piper [3], being about 16000 cm^{-1} . The expected two excited states cannot be resolved in the spectrum of its solution, but two overlapping shoulders centered at about 480 nm (20800 cm^{-1}) and 440 nm (22700 cm^{-1}) for the powder (Fig. 1(b)) might be then assigned as spin-allowed transitions of v_3 : $^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$ and v_4 : $^4T_{1g}(\text{F}) \rightarrow ^4A_{2g}(\text{F})$, respectively [3]. Another spin forbidden transition should be very low in energy, the lowest energy of $^4T_{1g} \rightarrow ^2E_g$ transition, as well as in intensity

should, therefore, be masked by the first spin-allowed transition, and consequently it is not observed.

Infrared Spectrum

The infrared spectrum of *bipy* has been recorded to compare with its corresponding various transitional metal complexes by Sinha [13] who observed that considerably shifted absorption bands of the characteristic groups of *bipy* have been identified due to chelation. This conclusion has also been confirmed by a number of references [14-16]. In the case of rare-earth metals of *bipy*, the shifted absorptions were observed at region 1470–1500, 1320, and 700–800 cm^{-1} . In the divalent metal complexes (Mn, Co, Ni) of *bipy* [15], the ring mode was observed at around 1600 cm^{-1} ($\nu_{\text{C-C}}$), 1570 cm^{-1} ($\nu_{\text{C-N}}$), 1020 cm^{-1} (*bipy* 'breathing'), and 715–770 cm^{-1} (C–H out of plane bend). In this work as shown in Fig. 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 [16] and also other divalent metals [15] and therefore it is associated with the chelation.

In the case of triflate ion, the infrared of some metallic triflate salts is used as a comparison [7]. Thus, as in Fig. 2, the corresponding infrared spectrum can be assigned readily. The bands at 571 and 517 cm^{-1} are deformation asymmetry of CF_3 and of SO_3 , respectively, and the bands at 771 and 640 cm^{-1} are likely deformation symmetry of CF_3 and SO_3 , respectively. The modes of vibrations observed at 1265 and 1149 cm^{-1} are to be SO_3 and CF_3 asymmetric stretching modes, while those at 1030 and 1225 cm^{-1} are SO_3 and CF_3 symmetric stretching modes, respectively. Therefore, the infrared

data strongly suggest that the complex of the sample should contain the chelation of *bipy* to cobalt(II) and uncoordinated triflate anion.

The Powder X-Ray Diffraction and Structural Analysis

The single crystal of cation $[\text{Co}(\text{bipy})_3]^{2+}$ with particular anions has been reported. For the double salt chromate-nitrate heptahydrate, $[\text{Co}(\text{bipy})_3](\text{CrO}_4)_{0.5}(\text{NO}_3)\cdot 7\text{H}_2\text{O}$, the crystal adopts monoclinic symmetry of the space group, $\text{C}2/c$ [12]. While for the perchlorate, $[\text{Co}(\text{bipy})_3](\text{ClO}_4)_2$, it is also monoclinic symmetry but different space group, $\text{C}12/c12(15)$ [4]. For the chloride dihydrate-ethanol, however, it adopts a hexagonal symmetry of the space group, $\text{P}6_522$ [17].

The different cell parameters for all those crystals might be due to a different method in growing crystal as well as different anions. From those facts, the powder X-ray diffraction of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2\cdot 8\text{H}_2\text{O}$ was then recorded, and the observed diffractogram together with

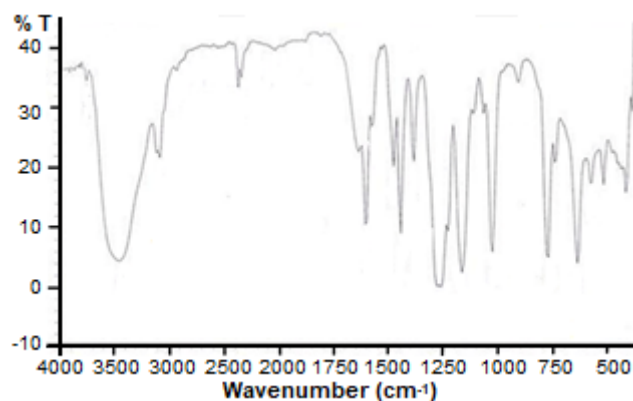


Fig 2. Infrared spectrum of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2\cdot 8\text{H}_2\text{O}$

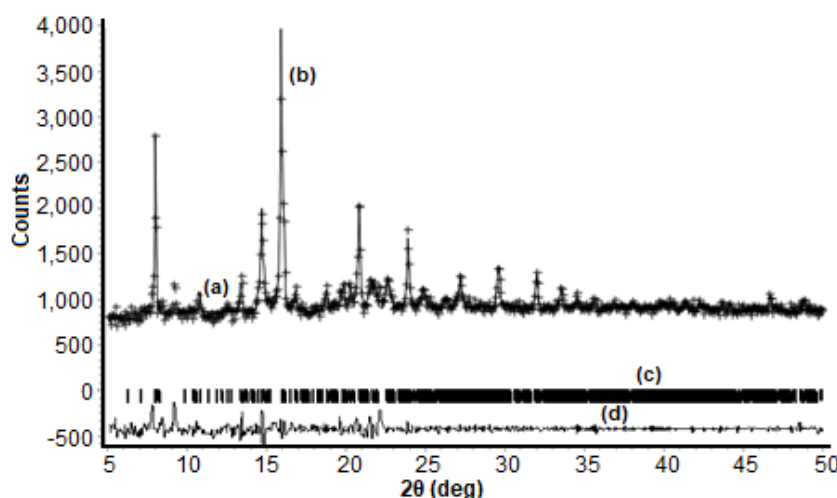


Fig 3. Diffractogram of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2\cdot 8\text{H}_2\text{O}$ (black sign +) (a), the refined monoclinic space group of $\text{C}2/c$ model (solid line) (b), with its bars-position of 2 theta (c), and the difference between the observed and the refined model (d)

Table 4. Detailed cell parameters of $[\text{Co}(\text{bipy})_3] \text{X}$ (*due to Le Bail method of Rietica program)

X	$(\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$ (This work)*	$(\text{CrO}_4)_{0.5}(\text{NO}_3) \cdot 7\text{H}_2\text{O}$ [12]	$(\text{ClO}_4)_2$ [4]	$\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ [17]
Symmetry	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space Group	C2/c	C2/c	C12/c12(15)	P6 ₅ 22
a (Å)	28.3991	24.325(5)	17.538(4)	13.403(2)
b (Å)	13.8964	13.974(3)	10.897(2)	-
c (Å)	22.2896	21.491(9)	16.078(3)	62.566(10)
V (Å ³)	8783.2304	7304(3)	3072.2	9733.6
α (°)	90	90	90	
β (°)	86.8444	91.11	91.01(3)	
γ (°)	90	90	90	
Z	4	8	4	12
R_p	2.77			
R_{wp}	6.24			
R_{exp}	1.63			
GOF	14.79	n.a	n.a	n.a
Bragg R-Factor	0.02			
GOF	14.65			

its refinement was shown in Fig. 3. The black signs (+) represent the observed experimental data, the solid line is the refinement according to Le Bail method of Rietica program (at 5–50 degree of 2 theta) for the expected model of monoclinic symmetry of space group C2/c which are the bars-lines (c), and the very bottom curve indicates the difference between the observed diffractogram and the refinement result.

It is clear that the solid line does almost pass through the observed data (signs +), and it is demonstrated by the almost flat of the very bottom curve, indicating that the corresponding refinement is almost fit with the cell parameters of $a = 28.3991 \text{ \AA}$, $b = 13.8964 \text{ \AA}$, $c = 22.2896 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 86.8444^\circ$, $\gamma = 90^\circ$, $V = 8783.2304 \text{ \AA}^3$, $Z=1$, $R_p = 2.77$, $R_{wp} = 6.24$ and $R_{exp} = 1.63$. The goodness of the fitting (GOF, 14.65), was also reflected by the derived Bragg R-Factor of 0.02. Detailed cell parameters of the crystal structure are presented in Table 4 together with known single crystal data of the same cation of the double salt of chromate-nitrate [12], of the perchlorate [4], and of the chloride complexes [17] as a comparison.

It should be noted that the application of Rietica program has not been performed to many powdered complexes. The first fitting might be applied to powdered of cobalt complex containing monodentate ammine by Zhu et al. [18]. It resulted in very low R factors, leading to 8.85 for GOF. The next application to be on powdered of cobalt complexes containing partially *bipy* in 2008 [19] with reasonably good fittings resulted in derived Bragg R-factors of 0.0048–0.0128 and GOF of 1.9–9.75. The powdered oxalate complexes [20] then have also been performed by Le Bail method and in fact, resulting in much higher 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 GOF. Recently, Sugiyarto et al. [21] reported the powder XRD for the complex of $[\text{Mn}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot 6.5\text{H}_2\text{O}$, with the R values of 3.67 (R_p), 7.34 (R_{wp}) and 3.61 (R_{exp}) leading to

GOF of 4.13, and 0.16 (R_{Bragg}). Quite recently, the powder XRD for the complex of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot (0.5-1) \text{H}_2\text{O}$ has been reported by Kusumawardani, Kainastiti and Sugiyarto [22], which resulted in the R values of 5.50 (R_p), 9.94 (R_{wp}) and 2.68 (R_{exp}) leading to GOF of 13.72, and 0.02 of R_{Bragg} . How low of R factors have been discussed in detail by Toby [23], however, it is in fact not so easy to conclude. It seems no acceptable limit of R's values could be concluded. For those reasons, the complex synthesized in this work might be considered to adopt monoclinic symmetry of the space group, C2/c.

CONCLUSION

The powder complex of $[\text{Co}(\text{bipy})_3](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$ has been successfully synthesized. It is a high-spin Co(II) with a significantly orbital contribution to the magnetic moment. The electronic spectral property of the complex reveals the main absorption band concentrated at about 900 nm (11110 cm^{-1}), which is attributed to the spin-allowed transition, ${}^4T_{1g} \rightarrow {}^4T_{2g}$. The infrared spectrum of the complex recorded at the range $500\text{--}4000 \text{ cm}^{-1}$ shows the typical vibration bands of characteristic groups of 2,2'-bipyridine and the corresponding triflate anion. The corresponding Powder X-Ray Diffraction analyzed using Le Bail method of Rietica program suggests that the complex adopt monoclinic symmetry of space group C2/c with the derived Bragg R-factor of 0.04.

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