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Contributed Paper

## Structural Analysis of Powder Tris(phenanthroline)nickel(II) Trifluoroacetate

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### ABSTRACT

The powder complex of tris(phenanthroline)nickel(II) trifluoroacetate has been synthesized by interaction of the corresponding nitrate salt in an aqueous solution and slightly excess of 1,10-phenanthroline in water/ethanol, whereupon the precipitate was produced on addition of an excess of saturated sodium trifluoroacetate solution while reducing the solvent. AAS measurement showed the content of metal to be 6.43 % being relatively close to the corresponding theoretical value of 6.60 % mass in  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$ . Moreover, the TGA confirmed the lost of 6.943% mass of complex corresponding to 3.43  $\text{H}_2\text{O}$ . The analysis of conductance producing the charge ratio of cation by anion to be 2:1, clearly confirms the formula. The magnetic moment,  $\mu_{\text{eff}}$  of this complex which was to be 3.19-3.31 BM, indicates that the complex is paramagnetic corresponding to two unpaired electrons which is clearly higher than the spin only value (2.87 BM) due to the spin-orbit coupling. UV-Vis spectrum of the complex revealed the first two main ligand field bands observed at about 12700 and 19250  $\text{cm}^{-1}$ , which are associated with the spin-allowed transition,  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ , respectively. The expected third band at higher energy was not well resolved due to the masked strong intensity of charge transfer band. The infrared spectrum shows absorptions of functional group of ligand which is influenced by the metal-ligand interaction in this complex. The powder XRD analysis of this complex was refined using Rietica-Le Bail method (within cycle number of 75) and found to be fit as monoclinic crystal system with space group of  $P2_1/M$ , and cell parameters of  $a = 12.8182 \text{ \AA}$ ,  $b = 30.8076 \text{ \AA}$ ,  $c = 16.7725 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 88.7349^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 6621.8145 \text{ \AA}^3$ ,  $Z=4$ , with figure of merit:  $R_p = 1.7$ ,  $R_{wp} = 4.08$  and  $R_{exp} = 0.32$ . The goodness of the fitting ( $\text{GOF} = 167.4$ ) was also reflected by the derived Bragg R-Factor of 0.06.

**Keywords:** Rietica, Le Bail, phen, trifluoroacetate, nickel(II)

### 1. INTRODUCTION

The chemistry of phenanthroline (*phen*) and catalysis have also been extensively discussed [1]. The single crystal of tris-phenanthroline nickel(II) perchlorate, the application in medicine, technology

$[\text{Ni}(\textit{phen})_3](\text{ClO}_4)_2$  has also been determined [2, 3]. It turns out that both which are the same formula is in fact demonstrating different in crystal structure, not only in the space group but consequently also in the corresponding cell parameters.

The preparation of a single crystal suitable for refining the structural data of particular complex is sometimes quite complicated and even unsuccessful. Rietica program of Le Bail method has been well known to refine the lattice parameters for so many hundreds or may be thousands of metal oxides [4-6] and found to be fit. Long time ago Zhu, Wu, and Le Bail himself in 1999 have also reported to apply the first fitting of the program to a complex of ammine [7] and found to be good result. Unfortunately, no continual application to other complexes were reported since then. Quite recently, Sugiyarto *et al* [8] and Kusumawardani *et al* [9, 10] reported the application of the program to the complex compounds.

Thus, preparing powder complex, recording the X-Ray powder diffractogram and then refining the corresponding cell parameters might be an alternative way to identify them. Trifluoro acetic acid, H-TFA, has been known as a strong acid, it is more than 100,000 times stronger than that of acetic acid due to the highly electronegative fluorine atoms and consequent electron-withdrawing nature of the trifluoromethyl group weakens the oxygen-hydrogen bond and stabilises the anionic conjugate base. The corresponding  $pK_a$  is about 0.23 compared to a  $pK_a$  of 4.76 for the acetic acid [11]. Thus, it might be considered in the same group of strong acids with  $pK_a$  less than one, such as hydroiodic, hydrobromic, hydrochloric, perchloric, chloric, nitric and (mono)sulfuric acids [12].

Thus, it might be expected that the corresponding salt of TFA would be possible as counter ionic role in any cationic complex formation rather than the coordinated one, so that the ionic complex might be synthesized. However, the 3d cationic transition complex of TFA has not been much observed, and it seems the only cationic *mercuracycle* [13] was found.

In fact the monodentate coordinated TFA to aurum [14] and to cobalt(II) in a polymer complexes were observed [15]. Complex of diisopropylammonium trioroacetate has also been synthesized and found to be monodentate coordinated TFA with hydrogen bonding of N-H...O [16]. With transition metals, Ru, Os, and Ir, hydrogen bonding of TFA were produced [17]. With the monodentate ligand of pyridine (*py*), some molecular complexes of  $M(\text{Py})(\text{CF}_3\text{CO}_2)$  where  $M=\text{Cu}(\text{II}), \text{Ni}(\text{II}),$  and  $\text{Co}(\text{II})$ , were isolated, indicating the coordinated TFA as a ligand rather than counter anion [18].

The previous works clearly involved monodentate organic ligands, and it is readily understood that the TFA might prefer to coordinate as anionic ligand also. Thus, by involving relatively strong coordinated bidentate ligand such as 1, 10-phenanthroline, the tendency of TFA to be mono/bi-dentate anionic ligand might be hindered and an cationic complex should result.

To study the nickel(II) complex containing 1,10-phenanthroline with TFA anion, therefore, should reveal either the ionic or molecular nature of the complex. Moreover, to the corresponding powder of the complex its lattice parameters might be then revealed by Rietica-Le Bail method, and these are the main purpose of this work.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The main chemicals, nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 1, 10-phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2$ ), sodium trifluoroacetate ( $\text{CF}_3\text{COONa}$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), calcium chloride ( $\text{CaCl}_2$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), nickel sulfate ( $\text{NiSO}_4$ ), and aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), Iron(III) chloride ( $\text{FeCl}_3$ ) were purchased from Sigma-Aldrich. All the reagents were used without further purification.

### 2.2 Preparation of tris(phenanthroline)nickel(II) TFA

The mixture containing 0.1 mmol  $\text{Ni}(\text{NO}_3)_2$  and 0.32 mmol phenanthroline in about 15 mL aqueous solution with drops of ethanol was well stirred and warmed till solution become clear. To this solution, an excess of saturated aqueous solution of  $\text{CF}_3\text{COONa}$  (0.4 mmol in 5 mL) was added. The mixture was concentrated on warming, whereupon the light-pink solid was deposited on cooling while scratching. It was then filtered, rinsed with a minimum of cold water, and then dried in exposure.

### 2.3 Physical Measurements

*Magnetism.* The magnetic susceptibility for powder samples were obtained at room temperature only by using *Magnetic Susceptibility Balance* (MSB) of Auto Sherwood Scientific 240V-AC 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 [19]. The corresponding effective magnetic moment ( $\mu_{\text{eff}}$ ) was then calculated from the corrected molar magnetic susceptibility following the general formula,  $\mu_{\text{eff}} = 2.828 \sqrt{\chi_M T}$  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 2×2 cm particular thin glass adhered with ethanol. The fitting was then placed in the cell holder and the spectrum was recorded at 200-1000 nm. The spectrophotometer UV-Vis Shimadzu 2400 PC Series was applied for solution. The infrared spectrum of the powdered sample which were pressed on the cell was recorded on an infrared Spectrophotometer FTIR ABB MB3000 at 500 - 4000  $\text{cm}^{-1}$ .

*Metal Content and Ionic Property.* The metal content in the sample was estimated based on the data recorded using an Atomic Absorption Spectrophotometer PinAAcle 900T Perkin Elmer model. While the ionic property was estimated by recording the electrical (equivalent) conductance by using a Lutron CD-4301 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,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NiSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{FeCl}_3$ , and  $\text{Al}(\text{NO}_3)_3$ , which were also recorded on the same instrument.

*TGA-DTA (Thermogravimetric Analysis and Differential Thermal Analysis).* It was performed to confirm the lost of materials contained in the compound. Thus, the loss of hydrated molecule of water and decomposition of complex was performed on Diamond (Perkin Elmer Instruments), and simultaneous TGA-DTA were obtained by a model NETZSCH STA 409C/CO thermal analyzer with in the rate of 10 °C/min.

*Powder X-Ray Diffraction.* The diffractogram of the powder complex was recorded by using a Rigaku Miniflex 600 40 kW 15 mA 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  $2\theta$ ) with interval of 0.04 steps per 4 seconds for 2 hours. The resulting diffractogram was then analysed by Rietica program of Le Bail method (5-60 degree of  $2\theta$ ) which was run within 75 cycles.

SEM-EDX (*Scanning Electron Microscopy with Energy Dispersive X-Ray*). The SEM images of the complex were recorded in JEOL JED-2300 model to confirm the crystallinity as well as the content of main elements.

### 3. RESULTS AND DISCUSSION

#### 3.1 Conductance, TGA-DTA and Chemical Formula of the Complex

The interactions of the ligand, phenanthroline, and the nickel(II) salt in

solution produced the light-pink cationic complex which could be precipitated on the addition of sodium trifluoroacetate in excess. The electrical equivalent conductance of this complex was recorded and compared to the well known ionic simple compounds in aqueous solution, and the result is shown in Table 1. It suggests that the corresponding value is clearly in the range of ionic compounds with three ions per molecule, and thus the possible empirical formula of  $[\text{Ni}(\text{phen})_n](\text{CF}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$  is then proposed for this powdered complex.

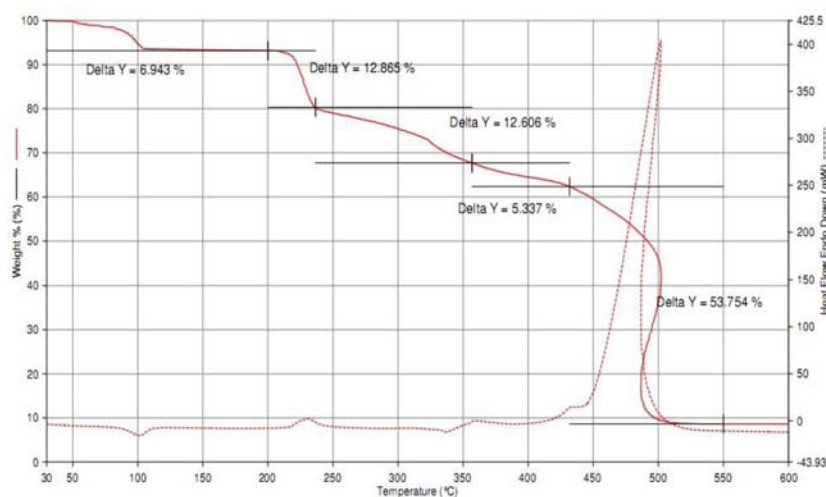
The coordination number of the empirical formula,  $n$ , was then estimated on the basis of metal content obtained from atomic absorption spectral data (calculated 6.60%, found 6.43%) as shown in Table 2, and the number of hydrated molecule of water,  $x$ , was confirmed by the data of mass loss following TGA-DTA graphs as shown in Figure 1.

**Table 1.** Electrical equivalent conductance of the complex and some known salts in aqueous solutions.

Compounds	Equivalent conductance ( $\Lambda\text{c}$ ) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Amount ratio of cation/anion	Number of ions per molecule
$\text{NH}_4\text{NO}_3$	160.429	1 : 1	2
$\text{NiSO}_4$	118.355	1 : 1	2
$\text{MnSO}_4$	119.612	1 : 1	2
$\text{CaCl}_2$	194.515	1 : 2	3
$\text{Ca}(\text{NO}_3)_2$	379.355	1 : 2	3
$\text{Al}(\text{NO}_3)_3$	519.095	1 : 3	4
$\text{FeCl}_3$	476.975	1 : 3	4
$[\text{Ni}(\text{phen})_n](\text{CF}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$	215.337	1 : 2	3

**Table 2.** Entity Found (w/w %) in  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$ .

Type	Ni	H <sub>2</sub> O	(CF <sub>3</sub> COO)	(phen)
Calculated	6.60	7.091	25.444	60.857
Found	6.43	6.943	25.471	59.091
Method	AAS	TGA	TGA	TGA

**Figure 1.** The TGA-DTA of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  at 30-600 °C.

The first stage of mass loss for 6.943% at about 100 °C should be associated with the loss of uncoordinated water molecules (being equal to 3.42 H<sub>2</sub>O) which is to be 7.0917% for 3.5H<sub>2</sub>O. This indication was also observed by Chandraleka and Chandramohan [20]. This suggests that the chemical formula of the complex would then be reasonably fit to be proposed as  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$ , being expected also from the stoichiometric preparation. Therefore the conductivity data of this complex confirms the ionic property of the TFA complex rather than the coordinated TFA [14-18].

The following two stages of loss in mass at the range of 200-360 °C, that is a two-stage loss in a total for about 25.471% might be considered due to loss of TFA as also observed by Eloussi *et al* [21]. This value

equals to 2.003 anionic TFA which is to be 25.444% for 2(CF<sub>3</sub>COO). The next loss of mass at 360-500 °C for about 59.091% should be associated with loss of phenanthroline which is to be 60.857% for 3(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>) in this instance. Laishram [22] proposed the loss of phenanthroline at 285-476 °C. The remaining observed to be 8.51% in fact corresponds to the calculated nickel oxide which is 9.05% in mass.

In summary, the comparison of percentage amount (in mass) for each entity between the calculation and experimental values in the complex were to be (found in bracket) Ni: 6.94 (6.43); H<sub>2</sub>O: 7.091 (6.943); 2[CF<sub>3</sub>COO]: 25.444 (25.471); 3[phen]: 60.857 (59.091), as also shown in Table 2. Thus in this instance, the complex was then characterized as  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$ .

### 3.2 Magnetic Moment

On the basis of the formula (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 3.19-3.31 BM. It is certainly higher than the spin-only value for the two unpaired electrons (2.83 BM) in the electronic configuration of Ni(II), and it is commonly observed due to orbital contribution by 'mixing in' of the wave-functions of the higher  $^3T$  terms [23, 24].

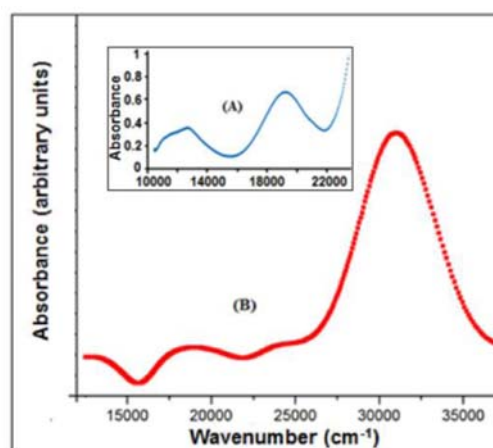
**Table 3.** Magnetic data of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  at 291 °C.

Sample	$\chi_M \cdot 10^{-6}$ (cgs)	$\mu_{\text{eff}}$ (BM)
1	4376.536	3.19
2	4707.815	3.31
3	4407.779	3.20

### 3.3 Electronic Spectrum

The electronic spectra of the aqueous solution (at 400-1000 nm) and powder (at 200-800 nm) of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  were recorded and in principle no different between the two, reflecting the stability of the complex in both states. As shown in Figure 2A (inset) for the solution, the two main ligand field bands were well resolved, centred at about 12500-12700 ( $\nu_1$ ) and 19200  $\text{cm}^{-1}$  ( $\nu_2$ ), being associated with the spin-allowed transitions of  $^3A_{2g} \rightarrow ^3T_{2g}$  and  $^3A_{2g} \rightarrow ^3T_{1g}(\text{F})$ , respectively. This spectrum is quite similar to that of the tetrafluoroborate recorded by Abramov [25], and the second band being responsible for the pink color. The extinction coefficient of 14.24 and 26.68  $\text{L mol}^{-1} \text{cm}^{-1}$  for the two respective bands are normal for octahedral environment. The expected third band,  $\nu_3(^3A_{2g}(\text{F}) \rightarrow ^3T_{1g}(\text{P}))$  as predicted by Tanabe-Sugano to be at higher energy was

not resolved in solution due to the masked strong intensity of charge transfer (MLCT) band. However, it seems to be at about 24000  $\text{cm}^{-1}$  for the solid (Figure 2B). While the highest and strongest band centred at about 31000  $\text{cm}^{-1}$  in the solid seems the charge transfer band.



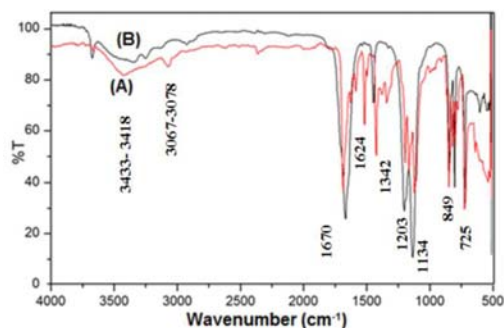
**Figure 2.** Electronic spectra of aqueous solution of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  (A, inset) and the powder (B).

### 3.4 Infrared Spectrum

The infrared spectrum of the complex was recorded and the main mode of vibrations are assigned by considering the infrared spectrum of sodium TFA which was overlaid as shown in Figure 3. Thus, the assignment seems straight forward. For the phenanthroline (Figure 3A-red) the broad band at about 3418 and 3433  $\text{cm}^{-1}$  might be due to -OH stretching of  $\text{H}_2\text{O}$  molecules as also observed by Shad *et al* at about 3441  $\text{cm}^{-1}$  [26], though Kumar *et al* [27] assigned C-C aromatic at 3430  $\text{cm}^{-1}$ . Another band at 3067-3078  $\text{cm}^{-1}$  should be due to stretching vibration of C-H bonds of phenanthroline which were observed by others at 3064  $\text{cm}^{-1}$  [2], and 3051-3068  $\text{cm}^{-1}$  [28]. In the range of 1650-1400  $\text{cm}^{-1}$ , four mode of vibrations according to Hu *et al* [2]

are characteristic of skeleton vibration of phenanthroline ( $\nu_{C-C}$  and  $\nu_{C-N}$ ), being to be at 1625, 1582, 1518, and 1425  $\text{cm}^{-1}$ , and in this instance, they are five, 1624, 1585, 1516, 1423 and 1342  $\text{cm}^{-1}$  ( $\nu_{C-N}$ ) [28]. While Abdelhak *et al* [29] proposed similarly that the mode of C-C would appear at that range, Zang *et al* [30] suggested that the mode of vibration at 1585  $\text{cm}^{-1}$  was to be  $\nu_{C-N}$ .

A very strong mode at 1686  $\text{cm}^{-1}$  might be due to C=O stretching as compared to that of sodium TFA (Figure 3B-black) which was observed at 1670  $\text{cm}^{-1}$ , while strong bands at 1203 and 1134  $\text{cm}^{-1}$  may be due to stretching of C-F and C-O, respectively. The bands at 725 and 849  $\text{cm}^{-1}$  are deformation asymmetry and symmetry of  $\text{CF}_3$ , respectively, [10] as observed in sodium TFA at 725-845  $\text{cm}^{-1}$ .



**Figure 3.** Infrared spectra of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  (A-red) and  $\text{CF}_3\text{COONa}$  (B-black).

### 3.5 The Powder X-Ray Diffraction and Structural Analysis

The single crystal of cation  $[\text{Ni}(\text{phen})_3]^{2+}$  with particular simple anions have been reported [2-3, 25]. While the both perchlorates adopt monoclinic symmetry [2, 3], they are surprisingly different in space group. The tetrafluoroborate monohydrate is triclinic symmetry [25]. Again surprisingly, another monoclinic single crystal of simple perchlorate

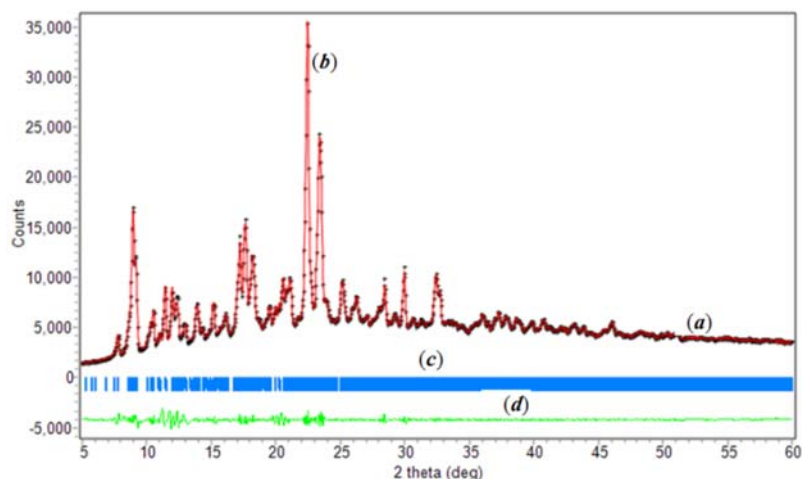
has also been reported [31] but as hemihydrate and with the same space group as in [3] and consequently the cell parameters being much the same within the two. On the other hand, another single crystal of the complex with simple bromide octahydrate has been refined [32] and found to be monoclinic. Based on those data the X-Ray powder diffraction of the complex of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  was then recorded and then refined according to Le Bail method. As shown in Figure 4, 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 fit with derived Bragg R-Factor of 0.06. Detailed results of cell parameters of the crystal structure are presented in Table 4 together with known single crystal data of the same cation, the tetrafluoroborate monohydrate [30], the perchlorate [2, 3], and the bromide [32]. For both perchlorate the first cell was elongated in *b* direction [2], and the second one was elongated in *a* direction [3] with the double volume of cell than the first one. This might cause to the double value of number of molecules in the second ( $Z=8$ ).

From Table 4, the figure merit of  $R_s$  values are considerably low and Bragg R-Factor close to 5%. However, the (square) ratio of  $R_{wp}/R_{exp}$  in fact leads to high value of GOF. How low the *R-factors* to be good enough is not easy to conclude as stated by Toby [33]. When GOF is close to one, there is no guarantee that the model is correct, there may be many models that will produce more or less equivalent fits, but the experimental data are not sufficient to produce a more complex and perhaps more correct model. It was also pointed out that if at the end of a refinement GOF is much more than 1, probably the model is reasonable but the s.u. values

are underestimated.

For comparison, the application of Le Bail method was performed on five oxalate complexes in 2009 [34]. The refined plot of powder diffractograms seem 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 GOF.



**Figure 4.** Diffractogram of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  (black sign +, **a**), and of refined monoclinic space group of  $P2_1/M$  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  $[\text{Ni}(\text{phen})_3] \text{X}$  where  $\text{X} = (\text{TFA})_2 \cdot 3.5\text{H}_2\text{O}$  (A)\*,  $(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (B),  $(\text{ClO}_4)_2$  (C),  $(\text{ClO}_4)_2$  (D),  $(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$  (E), and  $\text{Br}_2 \cdot 8\text{H}_2\text{O}$  (F) (\*This work due to *Le Bail* method of *Rietica* program).

X	(A)*	(B) [25]	(C) [2]	(D) [3]	(E) [31]	(F) [32]
Symmetry	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/M$	$P-1/2$	$P2_1/n$	$C2/c$	$C2/c$	$C2/m$
$a$ (Å)	12.8182	9.085(2)	9.388(2)	36.602(7)	36.714(4)	23.6320(11)
$b$ (Å)	30.8076	12.764(2)	30.139(5)	15.762(3)	15.746(2)	21.4880(13)
$c$ (Å)	16.7725	15.099(3)	12.974(2)	12.230(2)	12.337(2)	15.5470(9)
$V$ (Å <sup>3</sup> )	6621.8145	1734.1(1)	3426(1)	6882(2)	6952(3)	7511.5(7)
$\alpha$ (°)	90	95.84(1)	90	90	90	90
$\beta$ (°)	88.7349	90.48(1)	111.054(3)	102.75(3)	102.9(1)	107.927(3)
$\gamma$ (°)	90	95.23(1)	90	90	90	90
Z	4	2	4	8	8	8
<i>Figure of merit:</i>						
$R_p$	1.7					
$R_{wp}$	4.08					
$R_{exp}$	0.32					
Bragg R-Factor	0.06					
GOF	167.4	1.056	1.064	<i>n.a</i>	<i>n.a</i>	1.015



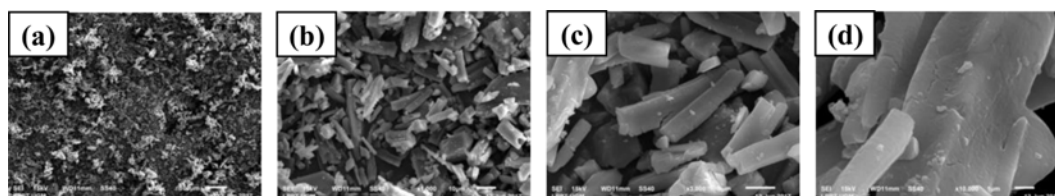
Thus, in this work the cell of the complex is elongated in *b* direction as also in the first perchlorate but with almost double volume of the cell though both contain the same number of molecules per cell ( $Z=4$ ). This could be due to different number of counter ions, the number of atom being seven in TFA with the 3.5 hydrated water molecules but 5 only in the perchlorate.

### 3.6 SEM-EDX

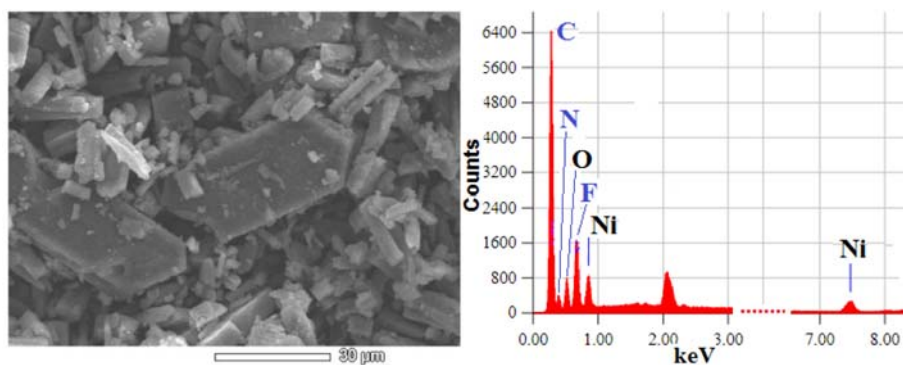
As shown in Figure 5, the SEM photographs of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  on various magnification reflects the high crystallinity of the complex as also

clearly demonstrated by the corresponding diffractogram which shows sharp peaks. Figure 5(d) might indicate monoclinic crystal system as resolved by the Rietica program on the diffractogram.

The corresponding energy dispersive X-ray (EDX) analysis result of the selected surface as shown in Figure 6 strongly demonstrates the existence of all elements except the hydrogen atom. Unfortunately, the percentage ratio of the number of atoms being Ni: 1(1.99%), C:27(54.40%), N:11.5(23.57%), O: 4.8(9.52%), and F: 5.3(10.51%) clearly does not reflect the accurate quantitative stoichiometry.



**Figure 5.** SEM photographs of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  at magnification of 100x (a), 1000x (b), 3000x (c) and 10,000x (d).



**Figure 6.** The image of selected surface of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  and its EDX analysis result showing the content of elements.

### 4. CONCLUSION

The powder complex of  $[\text{Ni}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 3.5\text{H}_2\text{O}$  has been successfully synthesized and characterized. The proposed formula of the complex was estimated by the measurements of electrical equivalent

conductance, and metal content (AAS), while the existence of hydrated water molecules, TFA ions and phenanthroline molecules were signified by TGA. The existence of elements were confirmed by EDX analysis. The magnetic moment was found to be

normal paramagnetic corresponding to two unpaired electrons with significant spin-orbit coupling. The electronic spectral property of the complex reveals the typical two main ligand field bands, both for the solution and the solid, but the third ligand field band as well as the charge transfer for the latter. The infrared spectrum of the complex shows the typical vibration bands of functional groups of phenanthroline and the corresponding TFA anion. The corresponding Powder X-Ray diffraction analysed using *Le Bail* method of *Rietica* program suggests that the complex adopt monoclinic symmetry of space group  $P2_1/M$ .

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