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Complex of Tris(phenanthroline)cobalt(II) Trifluoroacetate: Characterisation and Powder XRD Analysis

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ABSTRACT

The powder complex of tris(phenanthroline)cobalt(II) trifluoroacetate (TFA) has been prepared by interaction of cobalt(II) nitrate, phenanthroline (phen) in aqueous solution with drops of ethanol, and an excess of saturated aqueous solution of sodium trifluoroacetate, where upon the yellowish powder was produced. AAS measurment for the metal content, equivalent conductance (1:2), and TGA-DTA of the powder suggest the corresponding formula of $[Co(phen)_3](TFA)_2.5H_2O$. The efffective magnetic moment of 4.9 BM indicates the high-spin nature of this complex which corresponds to three unpaired electrons in the electronic configuration of Co(II) with significantly higher than the spin only value due to the orbital contribution. UV-Vis spectrum of the complex reveals the d-d spin-allowed transition bands as well as the MLCT and intraligand band. The estimating transition energy ratio of 2.04 for ν_2/ν_1, is clearly in the range for octahedral configuration. The infrared results property indicates the main mode of vibrations for the functional groups of ligand phen and TFA, and thus supports the formula proposed for this complex. The corresponding powder XRD was then refined using Rietica-Le Bail method and found to be fit as triclinic crystal system with space group of $P\bar{1}$.

Keywords: Rietica, Phen, Trifluoroacetate, Cobalt(II).

INTRODUCTION

Crystal structure of tris-bidentate-cobalt(II) complexes have been well known, particularly those with N-donor atoms in six-membered ring system, bipyridine *(bipy)*[1,2] and 1,10-phenanthroline *(phen)*[3]. Structural studies through single crystal XRD analyses of tris*(phen)*cobalt(II) with several counter anions, the *perchlorate* (ClO_4)[4], *squarate* (C_4O_4)[5], *tetrathionate* (S_4O_6)[6], *triiodide* (I_3)[7] and the *trichloroacetate* (CCl_3COO)[8] have been well refined. The point is that the cell parameters for the cationic complex in those complexes are different one to another even though the symmetry and space group of the crystal may or may not the same class. Therefore, discussing the cell parameters through other simple method by powder X-ray diffraction may be relevant. Quite recently, the cell parameters of some complexes have been estimated from the corresponding powder-XRD by applying Le Bail method[9-14], which is usually applied for powder metal oxides[15-18]. While in the absence of single crystal due to unsuccessful on producing them are quite often, the powder XRD offers an alternative way to estimate the cell parameters, and probably the position of atoms and thus bond lengths as well as bond angles might be depicted in one occation.

Salt of trifluoroasetate (TFA) has been known as strongly ionic nature due to highly electronegative fluorine atoms in the trifluoromethyl group.[19] The coordinating agent of oxygen atoms of acetate group to the transition metal ion has been known[20], however, it seems to diminish particularly when competing with other chelating bidentate ligands, Viz bipyridine and phenanthroline, in an octahedral configuration. Indeed, complexes of $[M(phen)_3](TFA)_2$ where M = Ni(II), Cu(II), and Mn(II)[12-14] have been characterized to be ionic.

Therefore, preparation of a complex containing cobalt(II), 1,10-phenanthroline and TFA should be of interest to confirm the role of TFA as a ligand or counter anion as well as structural study of the powder-XRD.

MATERIALS AND METHODS

Materials

The common reagents, cobalt(II) nitrate, 1,10-phenanthroline, sodium trifluoroacetate (NaTFA), ammonium nitrate, calcium chloride, calcium nitrate, and aluminium nitrate were purchased from Sigma-Aldrich, and used as they were recieved.

Preparation of tris-bipyridinecobalt(II) complex

A mixture of $Co(NO_3)_2$ (0.1 mmol) and phenanthroline (0.32 mmol) in about 15 mL aqueous solution with 2-3 drops of ethanol was well stirred and warmed till solution become clear. To this solution, an excess of saturated aqueous solution of CF_3COONa (0.5 mmol in 5 mL) was added. The resulting solution was concentrated on warming to about 8-10 mL, whereupon the yellow-orange powder was settled down on cooling while scratching. This solid was then filtered, rinsed with a minimum of cold water, and then dried in exposure. Preparation of this complex was seperately performed three times to confirm the reproducibility of this sample.

Instrumentation and Physical Measurements

Magnetic susceptibility for powder samples were measured at room temperature only using magnetic susceptibility balance (MSB) of Auto Sherwood Scientific 10169 model, calibrated with $MnCl_2$. The molar magnetic susceptibility data were then corrected for diamagnetism according to Pascal's constant.[21] The effective magnetic moment (μ_{eff}) was then calculated from the corrected molar magnetic susceptibility by the formula, $\mu_{eff} = 2.828 \sqrt{(_{\chi M.}T)}$ BM.

For the solid sample, the electronic spectrum was recorded on Pharmaspec UV 1700 spectrophotometer by spreading the powder on a 2x2 cm particular thin glass pasted with ethanol. The fitting was then set in the cell holder and the spectrum was recorded at 300-1000 nm. While the infrared spectra of the powder sample and sodium TFA were recorded on an infrared Spectrophotometer of FTIR Shimadzu Prestige 21 model at 600-4000 cm^{-1}.

Metal content in the complex was estimated using an Atomic Absorption Spectrophotometer of Shimadzu AA-6650 model, while the ionic property of complex was estimated by comparing the data of electrical (equivalent) conductance with those of known ionic solutions recorded in the same conductometer calibrated with an aqueous solution of 1 M potassium chloride at 25^0C.

The mass loss of hydrated molecule of water and further decomposition of complex was performed on Diamond Perkin Elmer Instrument, and simultaneous TGA-DTA were obtained by a NETZSCH STA 409C/CO thermal analyzer model with the rate of 10^OC/minute.

Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-DEX) of images for the complex were recorded on JEOL JED-2300 model to confirm the crystalinity as well as the presence of main elements in the sample.

Powder X-Ray diffraction of the complex was recorded using a Rigaku Miniflex Benchtop Diffractometer, CuKα (λ=1.5406 Å). The powder was spread on the glass plate which was then placed on the cell holder. The data of reflections was recorded in scan mode at 10-80 degree of 2θ with interval of

0.02 and rate of 10. The obtained diffractogram was then refined by Rietica program of Le Bail method (10-80 degree of 2θ) within 75 cycles.

RESULTS AND DISCUSSION

Conductance, TGA-DTA and Chemical Formula of the Complex

Interaction of light-pink cobalt(II) ions and colorless phenanthroline molecules in a mixture that produces a light yelowish color seems almost certainly a cationic complex, $[Co(phen)_n]^{2+}$. The addition of anionic TFA in excess should exert the precipitation of a complex containing TFA. The data of electrical equivalent conductance for this complex together with some known ionic simple compounds in aqueous solution as shown in Table 1 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 $[Co(phen)_n](CF_3COO)_2.xH_2O$ might be reasonably proposed for the complex. This data also confirms strongly the highly ionic property of the complex containing Co(II)-*phen*-TFA.

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

Compounds	Equivalent conductance (Λc) $\Omega^{-1}cm^2mol^{-1}$	Charge Ratio of cation/anion	Number of ions
NH_4NO_3	128.174	1 : 1	2
$CaCl_2$	196.898	2 : 1	3
$Ca(NO_3)_2$	229.292	2 : 1	3
$Al(NO_3)_3$	510.054	3 : 1	4
$Co(phen)_3(CF_3COO_3)_2.5H_2O$	198.341	2 : 1	3

The coordination number (*n*) for the empirical formula of this complex could be then initially estimated on the basis of metal content obtained from atomic aborption spectral data which was found to be 6.42%, the calculated metal content being 6.43% for n =3 and x = 5 (but 6.37% for n =3 and x = 5.5 and 6.50% for n = 3 and x = 4.5). This was then confirmed further by the loss of mass for each composing entity as indicated in TGA-DTA graphs shown in Fig. 1 and in Table 2. The graph consists of 5 stages of decomposition with the total marking figures of 89.529%, leaving residual percentage of 10.471%. Unfortunately, the last stage of decomposition shows clearly that TG curve lasts at about only 10.00% starting at 500°C, which corresponds to metal oxide, Co_2O_3 (cal. 9.06%)[5]. This means that marking figure of 8.565% for the first stage of mass loss seems to be slightly corrected becoming about 9.036%. This is due to loss of 5 molecules of H_2O (calculated 9.82%). Without specifying the detailed compounds of decompositions, the next stage of 24.748% at 200-300°C may correspond to loss of TFA (cal. 24.68%) as also observed in other complexes containing TFA[12-14,22] and the next stage of 56.216% at 300-500°C[5,11,13,23] seems due to loss of phenanthroline (cal. 59.04%).

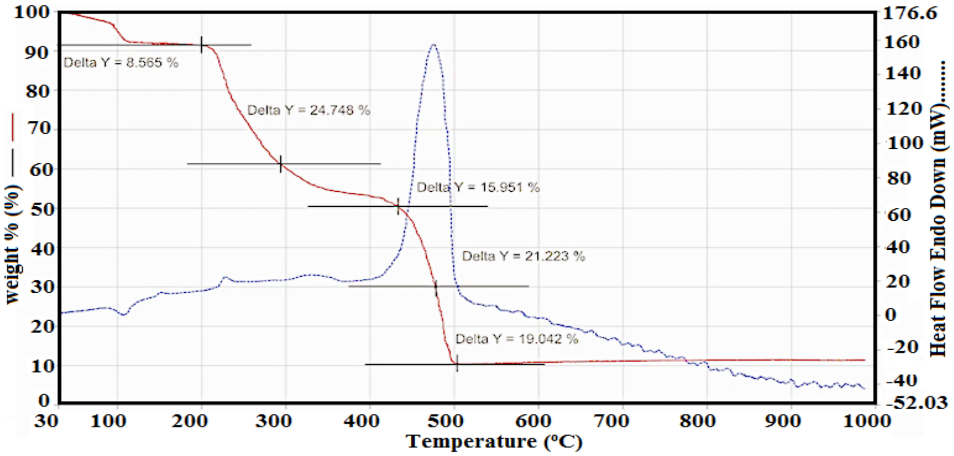

Fig. 1. The TGA-DTA of $[Co(phen)_3](CF_3COO)_2•5H_2O$ at 30-1000°C

Table 2: Composing entity contained in [Co*(phen)*$_3$](CF$_3$COO)$_2$.5H$_2$O

Type	Co	5H$_2$O	(CF$_3$COO)$_2$	*(phen)*3	½ Co$_2$O$_3$
Calculated	6.43	9.82	24.68	59.04	9.06
Found	6.42	9.036*)	24.748	56.216	10.00*)
Method	AAS	TGA	TGA	TGA	TGA
Error (%)	0.00	8.67	0.27	4.78	0.70

*) corrected figures; when the total 2nd -5th stage is 80.964%, for the residue to be 10.00% (see the graph in Fig.1), the corrected figure for 1st stage is then 9.036%

Magnetic Property

The magnetic susceptibility data obtained on measurement (Table 3) for the powder complex were then calculated to the magnetic moment on the basis of the formula proposed, and the result of the three separated samples are 4.89-4.90 BM, being similar to that found in the bromide counter anion[24], but slightly lower (4.3 BM) in the squarate counter anion[5]. These are definitely higher than that of spin only value for three unpaired electrons (3.87 BM) in high-spin 3d^7 configuration, due to the contribution to the moment which is quite commonly observed in Co(II) coplexes as predicted from the triply ground term of $^4T_{1g}$ in octahedral configuration[25,26]. Thus, phenanthroline produces clearly an octahedral weak ligand field surrounding Co(II).

Table 3: Magnetic data of [Co*(phen)*$_3$](CF$_3$COO)$_2$.5H$_2$O at 292K

Sample	$\chi_{M'}$ x 10^{-6} (cgs)	Magnetic Moment (BM)
1	10240	4.89
2	10310	4.90
3	10225	4.89

UV-Vis Electronic Spectrum

The electronic spectrum of the powder complex shown in Fig. 2 reveals the d-d transitions. The first broad absorption band of the lowest energy centred at about 930 nm (10750 cm^{-1}) is attributed to the spin-allowed transition, ν_1: $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), while the relatively sharp shoulder at 455 nm (21980 cm^{-1}) should be assigned as ν_2: $^4T_{1g} \rightarrow {}^4T_{1g}$(P), leading to the transition energy ratio ν_2/ν_1 = 2.04. This ratio is in the range 1.9-2.2 for octahedral configuration.[26] The broad shoulder centred at a lower energy, 675 nm (14800 cm^{-1}), might be then due to spin forbidden transitions, $^4T_{1g} \rightarrow {}^2\mathrm{T}_{1g}$; $^2T_{2g}$(G)[5,27]. When a two-electron transition in this complex is considered in near UV region, the ν_3: $^4T_{1g} \rightarrow {}^4\mathrm{A}_{2g}$(F) should be masked by the high intensity of metal-ligand charge transfer which appears sharply at 335 nm (29850 cm^{-1})[24]. Another sharp band at 257 nm (38900 cm^{-1}) is then to be $\pi \rightarrow \pi^*$ intra ligand transition[5]. For comparison, the diffuse reflectance spectrum of [Co*(phen)*$_3$](BF$_4$)$_2$ might be considered[27]. It shows some what different spectral pattern in terms of position of band peaks and in assigning the transitions which result in a slightly lower transition energy ratio, ν_2/ν_1 = 1.93. It is noted that its magnetic moment was also reported considerably lower, 4.03 BM in this instance.

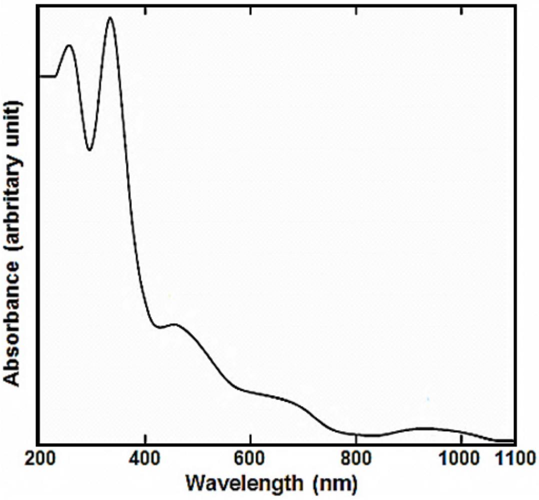

Fig. 2. Electronic spectrum of powder [Co*(phen)*$_3$](CF$_3$COO)$_2$•5H$_2$O

Infrared Spectrum

The infrared spectra of *phen* and the tris(*phenanthroline*)cobalt(II) complex have been known and reported to shift slightly in vibration modes due to chelation in the complex.[24] The infrared spectra of the complex prepared in this work and of the TFA anion were overlaid so as to assign straight forward as shown in Fig. 3. For the complex (Fig. 3A-red) a broad band at about 3400 cm^{-1} might be due to -OH stretching of H$_2$O molecule as observed at 3417 cm^{-1} according to Tao *et al.*,[3], but at 3512 cm^{-1} reported by Yesilel *el al.,*[5]. Another medium band at 3080 cm^{-1} is due to aromatic C-H bond as reported by Hamdani *et al.,*[28] at 3100 cm^{-1} and Zang *et al.,*[29] at 3064 cm^{-1}. Meanwhile, aromatic C=C is assigned at 1517 cm^{-1}, as observed by others[5,28,24] at 1516 cm^{-1}, 1518 cm^{-1}, and 1520 cm^{-1}. C-N mode of vibration is assigned at 1582 cm^{-1} as in Hamdani *et al.,*[28] but it was reported at 1627 cm^{-1} in Ramírez-Delgado *et al.*,[27]. In the case of TFA, a very strong mode at 1682 cm^{-1} might be due to C=O stretching[30] as compared to that of sodium TFA (Fig. 3B-black).

The bands at 867 and 800 cm^{-1} are to be asymmetry-symmetry deformation of CF_3, respectively.[30]

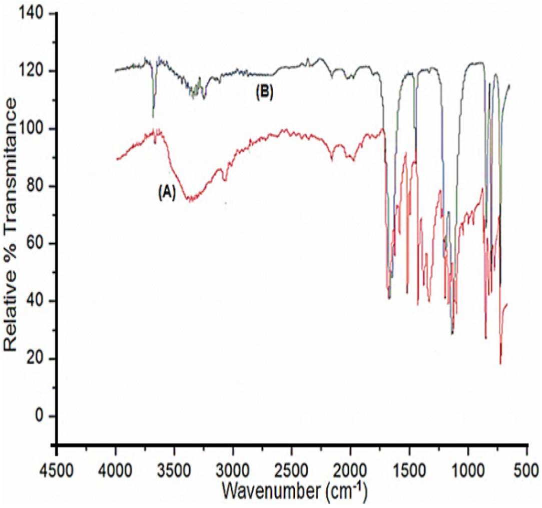

Fig. 3. Infrared Spectra of powder [Co*(phen)*$_3$] $(CF_3COO)_2$•$5H_2O$ (A, red) and CF_3COONa (B, black)

Therefore, the infrared data strongly suggest that the complex of sample should contain the chelation of phenanthroline ligand to cobalt(II) and (uncoordinated) TFA anion. Thus, all physical measurements of the complex support the proposed formula of the complex.

SEM-EDX

SEM images of the powder is depicted in Fig. 4 (a-c), and the related energy dispersive X-ray (EDX) analysis is shown in Fig. 4d. These signify crystalinity of the powder, and the presence of all elements composing the complex (except the hydrogen atom), C, N, F, O, and Co. It should be noted that the percentage ratio of the number of atoms does not represent the empirical formula of the complex, since it is not possible to have homogenous powder as indicated by the SEM images and its EDX.

Powder X-Ray Diffraction and Structural Analysis

The single crystals of cation [Co*(phen)*$_3$]$^{2+}$ with particularly various anions have been reported with cell parameters as shown in Table 4. They are [Co*(phen)*$_3$] X, where X = $(H_3btec)(H_2btec)_{0.5}$.DMF.$6H_2O$[3], (S_4O_6).$7H_2O$[6], $[C_4O_4]$.$8H_2O$[5], $(I_3)_2$[7], $(ClO_4)_2$•H_2O[4], and (CCl_3COO)[28]. They were found as triclinic-PI space group for the first two[3,6], monoclinic- $P2_1/c$ for the second two[5,7], and monoclinic-C_2/c for the last two[4,8], respectively. In fact, no cell parameters are found to be very close one to another although they are in the same symmetry and space group.

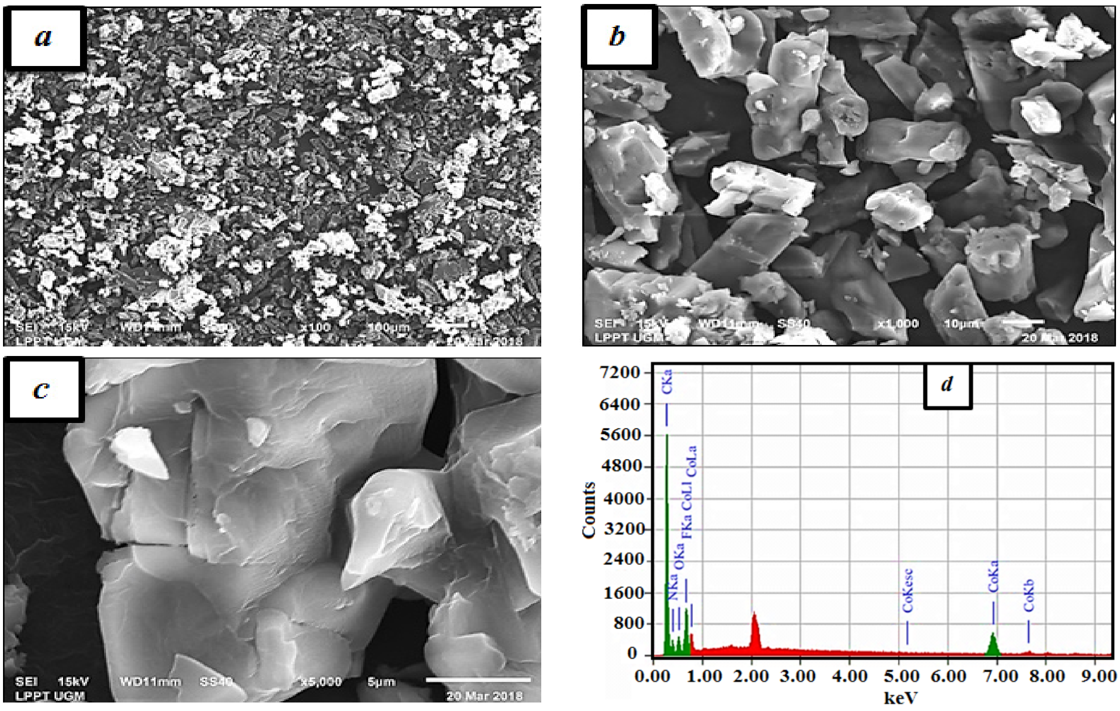

Fig. 4. SEM images of [Co*(phen)*$_3$]$(CF_3COO)_2$•$5H_2O$ at magnification of 100x (a), 1000x (b), and 5000x (c) and its EDX analysis result showing the content of elements, Co-C-F-N-O (d)

From those facts, the powder X-ray diffraction of [Co*(phen)*$_3$](CF$_3$COO)$_2$.5H$_2$O was then recorded and shown in Fig. 5 together with its refinement. The triclinic symmetry of space group PI was found considerably fit for this complex in this work. The red full line of the refinement according to Le Bail method of Rietica program (at 10-80 degree of 2 theta) is almost coincident with all the black signs (+) of the experimentally observed data. With the blue bar-lines corresponding to the position of peaks for the symmetry model, the difference between the observed data and the refinement was found nearly flat line (green). This is confirmed by the relative-low figures of merit of R_p = 2.01, R_{wp} = 3.11, R_{exp} = 1.91, and GOF = 2.646, with the derived Bragg R-Factor of 0.06. The cell parameters were found to be *a* = 12,3983 Å, *b* = 13.4523 Å, *c* = 14.3230 Å, α = 76.3580°; β = 67.3296°,γ = 70.7612^0 and V = 2064.905^0 Å^3, as shown in Table 4, together with known single crystal data for comparison. Thus, the symmetry-space group is quite similarly fit as to the tetrathionate, (S$_4$O$_6$).7H$_2$O[6] with cell parameters being quite close. Surprisingly, it is considerably different from the trichloroacetate[8], though both counter anions should adopt the same tetrahedral structure.

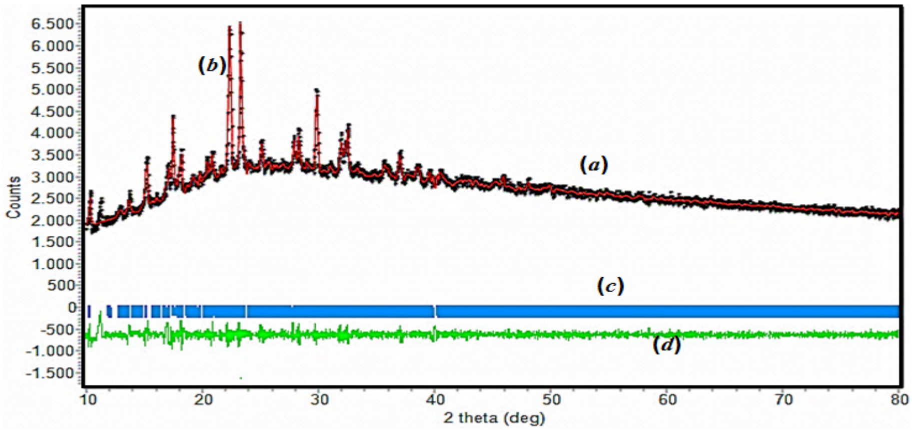

Fig. 5. Diffractogram of [Co*(phen)*$_3$](CF$_3$COO)$_2$•5H$_2$O (black sign +, *a*), and the refined triclinic space group of PI model (red full line, *b*) with it's posision of 2 theta of the model (blue bars, *c*), and the difference between the black observed and the red refined model (green, *d*)

Table 4: Detailed cell parameters of [Co*(phen)*$_3$]$^{X*, 3-8}$ (*due to *Le Bail* method of *Rietica* program)

X*,[3-8]	(CF$_3$COO)$_2$•5H$_2$O (This work)*	(S4O$_6$)•7H$_2$O[6]	(H$_3$btec)(H$_2$btec)$_{0.5}$ •DMF•6H$_2$O[3]	[C$_4$O$_4$]•8H$_2$O[5]	(I$_3$)$_2$[7]	(ClO$_4$)$_2$•8H$_2$O[4]	(CCl$_3$COO)$_2$[8]
Symmetry	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	PI	PI	PI	P2$_1$/c	P2$_1$/c	C*2*/c	C*2*/c
a (Å)	12.3983	12.4441	11.8123(14)	10.9832(5)	10.4187 (5)	36.366(12)	18.367 (4)
b (Å)	13.4523	13.1924	13.0356(16)	21.4569(12)	29.565 (1)	15.854(2)	10.753 (2)
c (Å)	14.3230	14.2385	17.575(2)	17.0649(7)	12.9299 (6)	12.341(1)	19.020 (4)
V (Å^3)	2064.9050	2018.77	2609.5(5)	3980.9(3)	3975.8 (3)	6938 (2)	3688.2 (13)
α (°)	76.3580	75.968	91.461(2)				
β (°)	67.3296	66.748	101.347(2)	98.159(3)	93.395 (10)	102.83 (2)	100.94 (3)
γ (°)	70.7612	71.562	99.830(2)				
Z	2	2	2	8	4	8	4
Figures of merit							
R_p	2.01						
R_{wp}	3.11						
R_{exp}	1.91						
GOF	2.46		1.029	0.918			
Bragg R-Factor	0.06						

CONCLUSION

The powder complex of [Co*(phen)*$_3$](CF$_3$COO)$_2$•5H$_2$O has been successfully prepared. The equivalent conductance confirms the ionic nature of this complex and the magnetic moment supports strongly the electronic configuration of high-spin Co(II) with three unpaired electrons, indicating an octahedral weak ligand field of tris-phenantroline ligand surrounding Co(II). The electronic spectral property of this complex reveals the *d-d* transitions with metal-ligand charge transfer (MLCT) and intraligand transition band. The infrared spectral property indicates clearly the main mode of vibrations of the ligand *phen* and TFA within the complex which support strongly formula of the complex. The corresponding powder X-ray diffraction which was analysed using Le Bail method of Rietica program suggests that the complex adopt triclinic symmetry of space group P$\bar{1}$.

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Conflict of Interest

The authors declare no conflict of interest in this writing.

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