



Structural Study of the Powder Complex of Cu(II)-1,10-Phenanthroline- Trifluoroacetate

KRISTIAN HANDOYO SUGIYARTO^{1*}, CAHYORINI KUSUMAWARDANI¹,
HESTINA WIGATI¹ and HARI SUTRISNO¹,

¹Department of Chemistry Education, Yogyakarta State University, Indonesia.

*Corresponding author E-mail: sugiyarto@uny.ac.id

<http://dx.doi.org/10.13005/ojc/350139>

(Received: November 12, 2018; Accepted: January 02, 2018)

ABSTRACT

The powder complex containing Cu(II), 1,10-phenanthroline (phen) and trifluoroacetate (TFA) has been obtained by single direct interaction of the corresponding precursors. The chemical formula of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{TFA})_2 \cdot 2\text{H}_2\text{O}$, diaquabis(phenanthroline)copper(II) trifluoroacetate dihydrate, has been proposed based on the TGA-DTA and the equivalent electrical conductance which was found in the range of 3 ions per molecule. The corresponding magnetic moment (μ_{eff} , 1.77-181 BM, supports that it is normal paramagnetic corresponding to spin-only value for an unpaired electron in the electronic configuration of Cu(II). UV-Vis spectrum of the complex reveals the only one broad absorption observed at about 681.50 nm (14673.51 cm^{-1}), being associated with the spin allowed transition, ${}^2E_g \rightarrow {}^2T_{2g}$. The infrared spectrum shows absorptions of ligand group which is influenced by the metal-ligand interaction in this complex. The powder XRD of this complex was refined by Le Bail method of Rietica program and found to be fit as triclinic symmetry of space group P1 with the cell parameters of $a = 10.8985 \text{ \AA}$; $b = 41.0532 \text{ \AA}$; $c = 16.1082 \text{ \AA}$; $\alpha = 98.2720^\circ$; $\beta = 91.9544^\circ$; $\gamma = 82.4071^\circ$; $V = 7068.8295 \text{ \AA}^3$; $Z = 1$; with figure of merit: $R_p = 1.83$; $R_{\text{wp}} = 5.70$; $R_{\text{exp}} = 0.37$; Bragg R-Factor = 0.03; and GOF = 231.4.

Keywords: Rietica, Le Bail, Phenanthroline, Trifluoroacetate, Copper(II).

INTRODUCTION

Trifluoroacetic acid, H-TFA, has been long known and considered as a strong acid since the pK_a value of about 0.23, being less than one as for perchloric, hydrochloric, chloric, and nitric acids¹. This reflects about 100,000 times stronger compared to acetic acid (with a pK_a of 4.76)². This characteristics might be due to the highly electronegative fluorine atoms which are more electron-withdrawing nature

in the trifluoromethyl group, and thus weakening the -COO-H bond. Hence, the corresponding potassium or sodium salts, might be a good source for counter anion rather than an oxygen-coordinating agent to the cationic metal complex. Unfortunately, not much anionic TFA of transitional metal complexes have been observed, and till quite recently it is true, for at least the synthesis of transition metal complexes of phenanthroline were reported by Sugiyarto *et al.*,³ and Sutrisno *et al.*⁴



Copper(II), is among other transition metals having a special preference of (4+2) coordination due to the Jahn-Teller effect⁵ associated with d⁹ electronic system⁶. Accordingly, the chemistry of copper(II) with various mono and bi-dentate ligands in the corresponding complexes have been well known to have coordination number of 4, 5 (square pyramidal and trigonal bipyramidal) and 6 as a result of the strong Jahn-Teller distortion.⁶⁻⁷

In the case of "symmetrical" bidentate ligands through nitrogen donor atoms, such as 2,2'-bipyridine and 1,10-phenanthroline, the corresponding bis-ligand mixed with another unsymmetrical bidentate of nitrogen-oxygen donor atoms, monodentate ligand, the six-coordination complexes of Cu(II) might result⁶. However, five-coordination either distorted square pyramidal or trigonal-bipyramidal geometry⁶⁻⁷ might also be produced. Thus, it should not be surprising, though it is certainly very rarely, when single crystal of tris-bipyridine copper(II) perchlorate in fact was observed to be two types, one a six-coordinated complex while the other a five-coordinated-distorted square-pyramidal geometry⁹. From this point, structural study of the lattice parameters which could be undoubtedly analysed from the powder X-Ray diffraction of the synthesized complex of [Cu-phen-TFA-H₂O], is then significant and this is the main point in this work.

MATERIALS AND METHODS

Materials

The essential chemicals of copper(II) nitrate, 1,10-phenanthroline (C₁₂H₈N₂), sodium trifluoroacetate, copper(II) sulfate, calcium chloride, mangan(II) sulfate, nickel sulfate, aluminium nitrate and iron(III) chloride were purchased from Sigma-Aldrich. All the reagents were used without any purification.

Preparation of copper(II) complex

About 10 mL of an aqueous solution of 0.1 mmol Cu(NO₃)₂ and 5 mL solution of 0.32 mmol phenanthroline in water (with drops of ethanol to dissolve) were mixed. The mixture was warmed while stirring to obtain an homogeneous solution. An excess of saturated aqueous solution of CF₃COONa (5 mL aqueous solution of 0.4 mmol) was then added to this solution. The mixture was concentrated on

warming, and the obtained powder on cooling was then separated by filtering, rinsed with a minimum of cold water, and then dried in exposure.

Instruments

Magnetic Moment. The magnetic susceptibility for the three powdered samples were recorded at room temperature using the Magnetic Susceptibility Balance (MSB) of Auto Sherwood Scientific 10169 model, which was calibrated with CuSO₄·5H₂O. After converted to molar magnetic susceptibility data it was then corrected with the diamagnetic values according to Pascal's constant¹⁰ to have the corresponding effective magnetic moments (μ_{eff}) following the formula, $\mu_{\text{eff}} = 2.828\sqrt{\chi_M T}$ BM.

Electronic and Infrared Spectra

The electronic spectrum of the powdered sample was recorded on Pharmaspec UV 1700 spectrophotometer, while in solution it was recorded on Spektrofotometer UV-Vis Shimadzu 2400 PC Series. The spectra were recorded at 400-1000 nm. For the infrared spectrum, the powdered sample was recorded on an infrared spectrophotometer FTIR Shimadzu Prestige 21 at 500 - 4000 cm⁻¹.

Ionic Characteristic

The ionic characteristic of the complex was estimated from the measurement of the electrical equivalent conductance by using a conductometer calibrated with an aqueous solution of 1 M potassium chloride at 25°C. The data obtained were estimated according to those of known ionic solutions, NiSO₄, MnSO₄, CuSO₄, CaCl₂, FeCl₃, and Al(NO₃)₃, which were simultaneously recorded with the same conductometer.

Powder XRD. The diffractogram of the powdered complex was recorded by using a Rigaku Miniflex Benchtop Diffractometer, CuK α : $\lambda=1.5406 \text{ \AA}$, in a scan mode at 2-90 degree of 2 θ at rate of 10 and an interval of 0.02. The resulted diffractogram was then analysed according to Rietica program of Le Bail method at 5-60 degree of 2 θ , which was run within 75 cycles.

RESULTS AND DISCUSSION

The Empirical Formula of the Complex

The blue precipitate produced on addition of saturated aqueous solution of sodium TFA in excess into the mixture containing phenanthroline and Cu(II) should result in the corresponding copper(II)

complex of phenanthroline-TFA. The equivalent electrical conductance of the complex in aqueous solution which was found to be in the range of 3 ions per molecule as compared to some other known samples (Table 1) suggests that TFA should act as counter anions. Hence, an empirical formula of $[\text{Cu}(\text{phen})_n(\text{H}_2\text{O})_m](\text{TFA})_2 \cdot x\text{H}_2\text{O}$ was proposed.

Table 1: The equivalent electrical conductance of the complex and some known salts in aqueous solutions

Compounds	Equivalent conductance (Λc) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Amount ratio of cation/anion	Number of ions per molecule
NiSO_4	118.355	1 : 1	2
MnSO_4	119.612	1 : 1	2
CuSO_4	114.770	1 : 1	2
CaCl_2	194.515	1 : 2	3
$\text{Al}(\text{NO}_3)_3$	519.095	1 : 3	4
FeCl_3	476.975	1 : 3	4
$[\text{Cu}(\text{phen})_n(\text{H}_2\text{O})_m](\text{TFA})_2 \cdot x\text{H}_2\text{O}$	150.125	1 : 2	3

This chemical formula was then estimated from the corresponding TG-DTA data. As shown in Fig. 1. The thermal decomposition of this complex takes place in four-five stages. By assuming the formula to be $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{TFA})_2 \cdot 2\text{H}_2\text{O}$ it suggests that the first loss of mass about 4.983% in the range 70-100°C likely corresponds to the thermal dehydration of uncoordinated water, which is calculated to be 4.986% for $2\text{H}_2\text{O}$.

The next stage of loss of mass takes place from about 170 to 315°C, it is 35.586%. In this curve of loss in mass, the first might be due to loss of coordinated water, it is 4.986% for $(\text{H}_2\text{O})_2$, while the next loss is likely the decomposition of $(\text{TFA})_2$ anions (cal. 31.30%) completed at 315°C, giving rise to the total theoretical loss of 36.286% in mass.

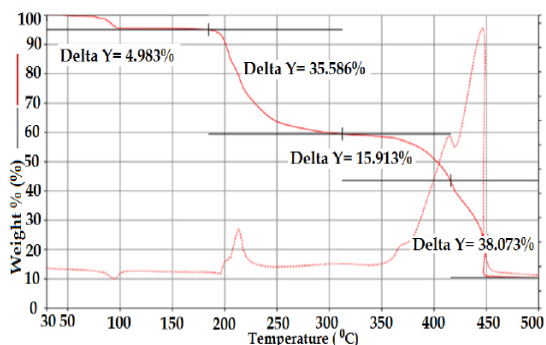


Fig. 1. The TGA-DTA of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{TFA})_2 \cdot 2\text{H}_2\text{O}$ at 30-500°C

The decomposition of coordinated water has been reported up to 190-200°C¹¹, and Chandrleka and Chandramohan reported at 90-200°C for decomposition of both uncoordinated and coordinated water, and it is a general way to distinguish the decomposition of lattice water molecules occurring in the range of 50-130°C from that of coordinated ones in the range of 130-250°C¹².

While for TFA it was decomposed in the range of 240-300°C¹³, 285-295°C¹⁴, and 240-320°C for coordinated TFA¹⁵. The following two stages 315-420-450°C might be then due to decomposition of two mole of phenanthroline one by one, and they are combined into 48.986%, being reasonable close to the theoretical calculation of 49.925%. As reported by Kharadi¹¹, decomposition of phen-ligand occurred at 265-350°C and 420-480°C¹¹.

The remaining 10.445% loss of mass at above 450°C should be due to CuO (cal. 11.01%). Table 2 summarizing data of theoretical calculation and observed TGA-DTA is thus reasonably confirmed the proposed formula.

Table 2: Observed and calculated data of TG-DTA

Type	2phen	2H ₂ O (L)	2TFA	2H ₂ O	CuO	Σ
Mr	360.42	36	226	36	79.54	721.92
TGA (%)	48.986	35.586	4.983	10.445	100	
Calculated (%)	49.925	4.986	31.30	4.986	11.01	100
		(36.286)				
Error (%)	1.88	1.92	0.06	5.13		

The Magnetic Moment

As shown in Table 3 the magnetic moment calculated from the measurement of the magnetic susceptibility of the estimated formula for three separately prepared samples was 1.77-1.81 BM, being normal paramagnet for the d^9 electrons of $\text{Cu}(\text{II})$. It is very close to the spin-only value (1.73 BM), which is quite common observed in $\text{Cu}(\text{II})$ -complexes^{7,12}, and no Cu-Cu interaction^{7,16,17}.

Table 3: Magnetic data of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

Sample	T (K)	$\chi_{\text{M}} \times 10^6$ (cgs)	Magnetic Moment (BM)
1	291	1.3362	1.78
2	291	1.3066	1.77
3	291	1.3944	1.81

The Electronic Spectra

The electronic spectrum of the complex in solution was recorded at 200-800 nm and shown in Fig. 2 (inset). It shows slightly asymmetric single broad band concentrated at about 677 nm (14770 cm^{-1}), indicating an octahedral distortion, being associated with Jahn-Teller effect⁵. This band might be attributed to the spin allowed transition of ${}^2E_g \rightarrow {}^2T_{2g}$ in copper(II) and this is slightly weaker than that of the tris-phen(Cu)-complex of perchlorate¹⁹, being 14850 cm^{-1} , but much stronger than that of the starting material, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (i.e. about 12000 cm^{-1})²⁰.

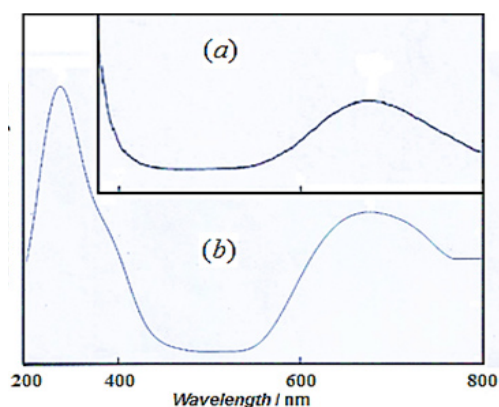


Fig. 2. Electronic spectra of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$: (a) in solutions (inset) and (b) powder

In powder-solid, the spectrum shows practically no change in position of this ligand field band, indicating the stability of this complex in both states. Another sharp band is concentrated at 337 nm (29670 cm^{-1}) with a distinct shoulder at lower energy around 400 nm (25000 cm^{-1}); they are phenanthroline ligand-metal charge transfer and intraligand $\pi-\pi^*$ transitions.^{16, 21}

The Infrared Spectrum

The IR spectra of the complex and TFA were recorded in the range 500-4000 cm^{-1} as overlaid and displayed in Fig. 3 and hence, it seems readily assigned. For the phenanthroline (A-red) the broad band at about 3418 - 3433 cm^{-1} might be due to -OH stretching of H_2O molecules²²⁻²⁴ as observed also by Sutrisno *et al.*,⁴ and reported by Shad *et al.*, at about 3441 cm^{-1} .²⁵ The vibration at about 3067 cm^{-1} may be assigned as modes of $\nu_{\text{C-H}}$ bond as reported by others^{26,27} at 3064 cm^{-1} , and 3051-3068 cm^{-1} . The modes of vibrations at 1624, 1602, 1516, and 1423 cm^{-1} might be assigned as the skeleton ring modes of $\nu_{\text{C-C}}$ and $\nu_{\text{C-N}}$ which are in the range of

1650-1400 cm^{-1} as also reported by Hu *et al.*,²⁶ and also Abdelhak *et al.*,²⁸ though Zang *et al.*,²⁹ suggested that the mode of vibration at 1585 cm^{-1} was due to $\nu_{\text{C-N}}$.

The remaining modes at 1670, 1443, 1203, 1134, 849, 802, 725, are to be primarily due to the TFA characters.³ They are assigned as C-O, C-C stretchings, and asymmetry-symmetry deformation of CF_3 .

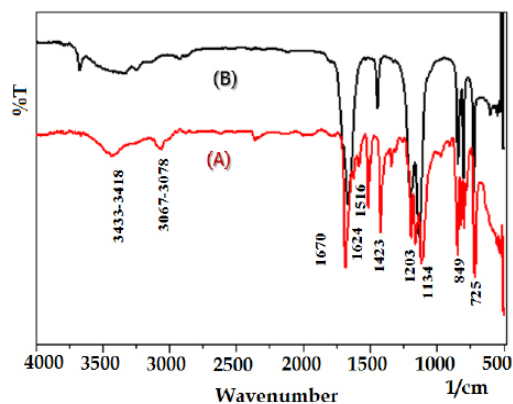


Fig. 3. Infrared spectra of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (A-red) and CF_3COONa (B-black) with numbers of selected bands

The Powder XRD and Structural Analysis

The powder X-ray diffraction of the complex $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was then recorded, and the diffractogram together with its refinement following Le Bail method of Rietica program is shown in Fig. 4. The black signs (+) represent the observed-experimental data, the full line (red) is the refinement at 5-60 degree of 2 theta for the expected model of triclinic symmetry of space group P1 which are the blue bar-lines, and the green curve-line indicates the differences between the observed diffractogram and the refinement.

It is obvious that the red full line does almost pass through the black observed data, and this is demonstrated by the green-curve which is almost flat, indicating that the corresponding refinement might be considered very good with the Goodness of Fitting (GOF) to be 231.4 with derived Bragg R-Factor of 0.03, and low figure of merit: $R_p = 1.83$; $R_{wp} = 5.70$; $R_{exp} = 0.37$. Detailed results of lattice parameters of the crystal structure are presented in Table 4, together with the known single crystal data of others related complexes for comparison.

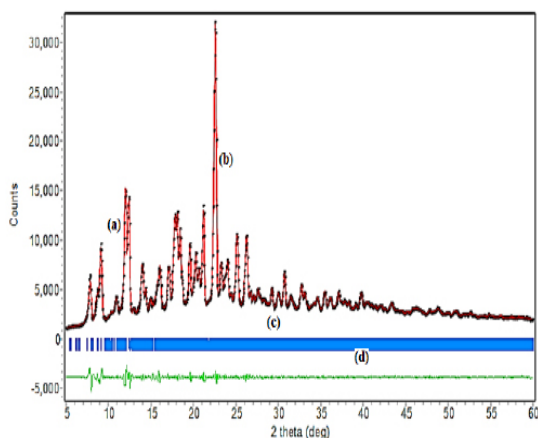


Fig. 4. Diffractogram of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (black sign +, a), and of refined triclinic space group of P1 model (red full line, b) with its position of 2 theta (blue bars, c), and the difference between the black observed and the red refined model (green, d)

Lattice parameters of related complexes containing triflate anion might be considered for comparison. Thus, a single crystal of the triflate monohydrate²², $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$, has been reported and it was found to be triclinic system of a P1 space group. While for the corresponding powdered dihydrates, $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ ²⁰ the powder X-ray diffractogram has been refined to be the same triclinic system and P1 space group though both different in lattice parameters. Other powdered uncoordinated-TFA in the divalent complexes may also be usefull for comparison, they are $[\text{Mn}(\text{phen})_3](\text{TFA})_2 \cdot 1.35\text{H}_2\text{O}$ ³ and $[\text{Ni}(\text{phen})_3](\text{TFA})_2 \cdot 3.5\text{H}_2\text{O}$ ⁴. The refinement for both complexes were found to be very

good fittings, being structurally triclinic symmetry of PI for the former cationic complex with the cell parameters as shown in Table 4 with relatively low figure of merit of : $R_p = 1.31$; $R_{wp} = 2.39$; $R_{exp} = 0.56$; Bragg R-Factor = 0.04; and GOF = 18.00. For the latter complex, the low figures of merit are $R_p = 1.7$, $R_{wp} = 4.08$, $R_{exp} = 0.32$, GOF = 167.4 and derived Bragg R-Factor of 0.06. Thus, the structural analysis of Rietica program applied in powdered difragtogram of complex compounds seem acceptable. So, as shown in Table 4, it is clear that the triclinic symmetry for each complex shows difference in length of a-b-c axes. In this work, b axis was found to be much longer than a and b as observed also in Cu-phen-triflate.²⁰

How good is good enough of the fitting, Toby (2006)³⁰ discussed regarding how low of R factors and in fact it was found not easy to conclude. As quite recently reported by Kusumawardani *et al.*, (2017)²⁰, the R factors for powder of $\text{Cu}(\text{bipy})_3(\text{CF}_3\text{SO}_3)_2 \cdot (0.5-1) \text{H}_2\text{O}$, were found to be 5.50 (R_p), 9.94 (R_{wp}) and 2.68 (R_{exp}) leading to GOF of 13.72, and 0.02 (R_{Bragg}).

From these reasons, the complex in this work might be considered to have a space group of P1 in triclinic symmetry, and in principle it should be possible and promising to draw the molecular structure of the (cationic) complex extracted from the *hkl* produced by the fitting, though, it is still very hard struggling.

Table 4: Detailed cell parameters of $[\text{Cu}(\text{phen})_3]\text{X}$, where X = $(\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ (a), $(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ (b)²², $(\text{S}_4\text{O}_6)_2 \cdot 5\text{H}_2\text{O}$ (c)³¹, $(\text{TCNQ})_2 \cdot 0.5 \text{C}_2\text{H}_5\text{OH}$ (d)³² $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (e)*, and $[\text{Mn}(\text{phen})_3](\text{CF}_3\text{COO})_2 \cdot 1.35 \text{H}_2\text{O}$ (f); *)This work; (a, e and f) are due to Le Bail method of Rietica program

(X)	(a)	(b)	(c)	(d)	(e)*	(f)
Symmetry Space Grup	Triclinic P1	Triclinic P1	Triclinic P1	Triclinic P1	Triclinic P1	Triclinic P1
a (Å)	9.96201	10.7448(3)	11.232(4)	21.945(5)	10.8985	13.6422
b (Å)	39.89891	13.4992(3)	13.569(6)	11.106(3)	41.0532	18.2792
c (Å)	17.19187	14.8755(4)	14.654(6)	10.186(3)	16.1082	23.8741
V (Å ³)	6776.3286	1897.10(8)	2012.6(14)	2450.4	7068.8295	5261.6714
α (°)	95.92929	104.1650(10)	99.67(1)	86.50(5)	98.2720	114.4245
β (°)	86.18185	104.2840(10)	99.44(1)	84.41(6)	91.9544	94.8337
γ (°)	92.65168	105.7230(10)	109.75(1)	83.21(4)	82.4071	99.7977
R_p	5.19				1.83	1.31
R_{wp}	10.65				5.70	2.39
R_{exp}	1.99				0.37	0.32
Z	4	2	2	2	1	1
GOF: χ^2	28.58	1.046	n.a	n.a	231.4	18
R_{Bragg}	0.03				0.03	0.04

The SEM-EDX

The high crystallinity of the powder-complex as reflected by the sharp peaks of the diffractogram (Fig. 4) was confirmed by the corresponding SEM-photographs (Fig. 5) on various magnifications. The analysis of the corresponding energy dispersive X-ray (EDX) of the selected surface as shown in Fig. 6 strongly demonstrates the existence of all main elements, Cu-C-N-O-F, except the hydrogen atom, though it is not possible to estimate accurately the percentage of each element according to empirical formula of the complex.

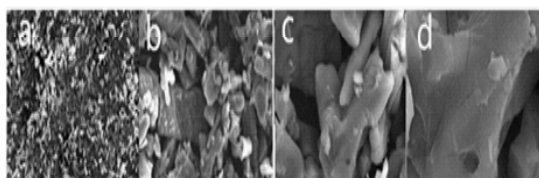


Fig. 5. SEM-photographs of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at magnification of 100x (a), 1000x (b), 3000x (c) and 10,000x (d)

CONCLUSION

The powder complex of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ has been prepared. The magnetic moment was found to be normal paramagnet for an unpaired electron of Cu(II). The electronic spectral property of the powder shows a slight asymmetry band concentrated at about 677 nm (14770 cm^{-1}), which is commonly attributed to the spin allowed transition, ${}^2\text{E} \rightarrow {}^2\text{T}_2$. The M-L and interligand charge transfer bands were also observed. The infrared spectrum of the complex shows the typical vibrations of the functional groups of phen and the corresponding uncoordinated triflate anion. The

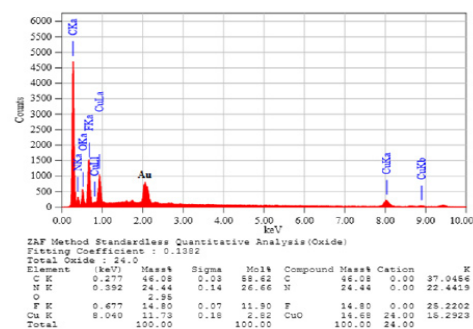
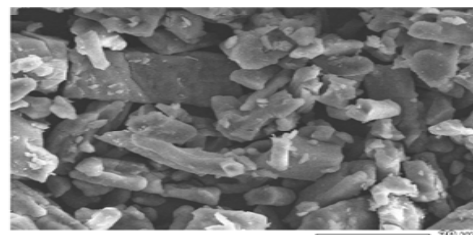


Fig. 6. The image of selected surface of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and its EDX analysis result showing the content of elements

Powder XRD refined by Rietica program of Le Bail fitting suggests that the complex is likely triclinic symmetry of space group P1 with the derived Bragg R-factor, 0.03.

ACKNOWLEDGMENT

The authors thank to the Faculty of Mathematics and Natural Science, YSU, due to the funding of DIPA-2017 for this work.

CONFLICT OF INTEREST STATEMENT

We declare that we have no conflict of interest in this article.

REFERENCES

1. Table of Acids with Ka and pKa Values (Compiled from Appendix 5 Chem 1A, B, C Lab Manual and Zumdahl 6th Ed. The pKa values for organic acids can be found in Appendix II of Bruice 5th Ed.). Retrieved from: <http://clas.sa.ucsb.edu/staff/Resource%20folder/Chem109ABC/Acid,%20Base%20Strength/Table%20of%20Acids%20w%20Kas%20and%20pKas.pdf>.
2. Trifluoroacetic Acid. Retrieved from: http://www.commonorganicchemistry.com/Common_Reagents/Trifluoroacetic_Acid/Trifluoroacetic_Acid.htm.
3. Sugiyarto, K. H.; Kusumawardani, C.; Sutrisno, H.; Wibowo, M. W. A. *Orient. J. Chem.*, **2018**, *34*(2), 735-742. DOI: [org/10.13005/ojc/340216](https://doi.org/10.13005/ojc/340216).
4. Sutrisno, H.; Kusumawardani, C.; Rananggana, R. Y.; Sugiyarto, K. H. *Chiang Mai J. Sci.*, **2018**, *45*(x), 1-11. Accepted to be published on 12 February 2018. <http://epg.science.cmu.ac.th/ejournal/>.
5. Babu, B. K.; Elahi, S. M.; Chary, T. K.; Rajasekharan, M. V. *Indian J. Chem. Sec. A.*, **2011**, *50A*, 1318-1323. <http://nopr.niscair.res.in/handle/123456789/12778>.

6. Syntheses and characterization of Cu(II) complexes of tridentate acylhydrazones; Chapter 5. Retrieved from: http://shodhganga.inflibnet.ac.in/bitstream/10603/6270/9/09_chapter%205.pdf.
7. Carballo, R.; Covelo, B.; Balboa, S.; Castiñeiras, A.; Niclós, J. Z. *Anorg. Allg. Chem.*, **2001**, *627*, 948-954. [https://doi.org/10.1002/1521-3749\(200105\)627:5<948::AID-ZAAC948>3.0.CO;2-3](https://doi.org/10.1002/1521-3749(200105)627:5<948::AID-ZAAC948>3.0.CO;2-3).
8. Anderson, O. P. *J. C. S. Dalton.*, **1972**, 2597-2601. DOI: 10.1039/DT9720002597.
9. Liu, Z. M.; Jiang, Z. H.; Liao, D. Z.; Wang, G. L.; Yao, X. K.; Wang, H. G. *Polyhedron.*, **1991**, *10*, 101-102. DOI: 10.1016/S0277-5387(00)83554-8.
10. Figgis B. N. and Lewis, J., *Modern Coordination Chemistry*, Edited by Lewis, J., and Wilkins, R. G., Interscience: New York., **1960**, 400.
11. Kharadi, *J. Therm. Anal. Calorim.*, **2012**, *107*, 651-659; DOI: 10.1007/s10973-011-1671-x
12. Chandraleka, S.; Chandramohan, G. *Afr. J. Pure Appl. Chem.*, **2014**, *8*(10), 162-175. DOI: 10.5897/AJPAC2014.0592.
13. Llordes, A.; Zalamova, K.; Ricart, S.; Palau, A.; Pomar, A.; Puig, T.; Hardy, A.; Van Bael, M. K.; Obradors, X. *Chem. Mater.*, **2010**, *22*, 1686-1694. DOI:10.1021/cm903080k./
14. Mishra, S.; Jeanneau, E.; Bulin, A. L.; Ledoux, G.; Jouguet, B.; Amans, D.; Belsky, A.; Daniele, S.; Dujardin, C. *Dalton Trans.*, **2013**, *42*, 12633-12643; DOI: 10.1039/c3dt50605c.
15. Dawley, J. T., Clem, P. G., Boyle, T. J., Ottley, L. M., Overmyer, D. L.; Siegal, M. P. *Physica C.*, **2004**, *40*, 143-151; DOI:10.1016/j.physc.2003.09.072.
16. Hazra, M.; Dolai, T.; Pandey, A.; Dey, S. K.; Patra, A. *Bioinorg. Chem. Appl.*, **2014**, Article ID 104046, 13 pages. <http://dx.doi.org/10.1155/2014/104046>.
17. Cotton, F. A. and Wilkinson, G. (Eds). *Advanced Inorganic Chemistry*, 5th ed. Wiley, New York., **1988**.
18. Devereux, M.; McCann, M.; Cronin, J. F.; Ferguson, G.; McKee, V. *Polyhedron.*, **1999**, *18*(16), 2141-2148. DOI: 10.1016/S0277-5387(99)00100-X.
19. Majumdar, P.; Ghosh, A. K.; Falvello, L. R.; Peng, S. M.; Goswami, S. *Inorg. Chem.*, **1998**, *37*, 1651-1654. DOI: 10.1021/ic970819m.
20. Kusumawardani, C.; Permanasari, L.; Fatonah, D. S.; Sugiyarto, K. H. *Orient. J. Chem.*, **2017**, *33*(6), 2841-2847. doi.org/10.13005/ojc/330617.
21. Chen, B. H.; Yao, H. H.; Huang, W. T.; Chattopadhyay, P.; Lo, J. M.; Lu, T. H. *Solid State Sci.*, **1999**, *1*(2-3), 119-131. [https://doi.org/10.1016/S1293-2558\(00\)80069-2](https://doi.org/10.1016/S1293-2558(00)80069-2).
22. Sletten, J.; Julve, M. *Acta Chem. Scand.*, **1999**, *53*, 631-633. DOI: 10.3891/acta.chem.scand.53-0631.
23. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Fifth Edition, Wiley, New York., **1997**, *53* and refs. therein.
24. Sinha, S. P. *Spectrochim. Acta.*, **1964**, *20*, 879-886. [https://doi.org/10.1016/0371-1951\(64\)80086-2](https://doi.org/10.1016/0371-1951(64)80086-2).
25. Shad, H. A.; Thebo, K. H.; Ibupoto, Z. H.; Malik, M. A.; O'Brien, P.; Raftery, J. *J. Coord. Chem.*, **2011**, *64*(13), 2353-2360. DOI 10.1080/00958972.2011.595789.
26. Chen, H.; Xu, X. Y.; Gao, J.; Yang, X. J.; Lu, L. D.; Wang X. *Acta Phys. Chim. Sin.*, **2006**, *22*(7), 856-859. DOI 10.3866/PKU.WHXB20060717.
27. Tosoniani, S.; Ruiz, C. J.; Rios, A.; Frias, E.; Eichler, J. F. *Open J. Inorg. Chem.*, **2013**, *3*(1), 7-13. DOI: 10.4236/ojic.2013.31002.
28. Abdelhak, J.; Cherni, S. N.; Zid, M. F. *Mediterr. J. Chem.*, **2014**, *3*(1), 738-745. DOI: 10.13171/mjc.2014.26.03.22.
29. Zang, J.; Wang, L. X.; Zang, L.; Chen, Y.; Zang, Q. T. *Rare Met.*, **2013**, *32*(6), 599-604. DOI: 10.1007/s12598-013-0168-0.
30. Toby, B. H. *Powder Diffr.*, **2006**, *21*(1), 67-70. <https://doi.org/10.1154/1.2179804>.
31. Freire, E.; Baggio, S.; Baggio, R., Garland, M. T. *Acta Crystallogr., Sect. C.*, **1998**, *54*, 464-468. <https://doi.org/10.1107/S0108270197016284>
32. Bencini, A.; Midollini, S.; Zanchini, C. *Inorg. Chem.*, **1989**, *28*, 1963-1969. DOI: 10.1021/ic00309a039