

Tony Blair Institute for Global Change  
Trinity University, Lagos, Nigeria  
Harmarth Global Educational Services  
FAIR Forward – Artificial Intelligence for All  
Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH  
Society for Multidisciplinary & Advanced Research Techniques (SMART)



---

---

32<sup>nd</sup> Accra Multidisciplinary Cross-Border Conference (AMCBC)

---

---

## Spectral and Antimicrobial Studies of Mixed Ligand Copper(II) Complexes with 1,1,1-Trifluoroacetylacetone and Nitrogen Containing Ligands

**Omoregie, Helen Oluwatola**  
Department of Chemistry  
University of Ibadan  
Ibadan, Oyo-State, Nigeria  
**E-mail:** tolaomoregie@gmail.com

### ABSTRACT

The mixed-ligand complexes of copper(II) with 1,1,1-trifluoroacetylacetone (TFA-H), 1,10-phenanthroline (phen), and 2,2'-bipyridine (bipy) have been synthesized and characterized by metal analysis, infrared spectra, electronic spectra, magnetic susceptibility measurements and antimicrobial activities. The infrared spectra of the complexes showed shift to lower absorption frequency bands in the carbonyl stretching frequencies on complexation. The electronic spectra measurements are corroborative of a probable five coordinate square pyramidal geometry for the copper(II) complexes. The room-temperature magnetic data obtained ranged between 1.76 and 2.23 B.M. for mixed-ligand copper(II) complexes. The antimicrobial activities carried out on the mixed-ligand copper(II) complexes showed that [Cu(TFA)PhenNO<sub>3</sub>] and [Cu(TFA)PhenCl] compared favourably well with Ketoconazole on *Candida albicans* and *Penicillium notatum* respectively.

**Keywords:** Antimicrobial, 1,1,1-trifluoroacetylacetone, 1,10-phenanthroline, 2,2'-bipyridine, Spectra, Copper (II),

---

---

#### Proceedings Citation Format

Omoregie, Helen Oluwatola (2022): Spectral and Antimicrobial Studies of Mixed Ligand Copper(II) Complexes with 1,1,1-Trifluoroacetylacetone and Nitrogen Containing Ligands. Proceedings of the 32<sup>nd</sup> Accra Multidisciplinary Cross-Border Conference. University of Ghana/Academic City University College, Ghana. 29<sup>th</sup> June-1<sup>st</sup> July, 2022. Pp 43-50  
[www.isteams.net/ghanabespoke2022](http://www.isteams.net/ghanabespoke2022).  
[dx.doi.org/10.22624/AIMS-/AMCBC2022P5](https://doi.org/10.22624/AIMS-/AMCBC2022P5)

---

---

## 1. INTRODUCTION.

Bacteria have developed resistance to drugs by various methods like the acquisition of new genetic material from other resistance organisms, gaining gene encoding enzymes and many more. The remedy to these problems has cut through diverse researches such as producing completely new drugs, modification of the existing ones, to mention a few<sup>[1,2,3]</sup>.

$\beta$ -diketones are very important compounds in organic chemistry since they exhibit some interesting biological activities, such as antiulcer, antioxidants, antitumor, antibacterial and antidiabetic activities<sup>[4]</sup> and are also key intermediate to various heterocyclic compounds<sup>[5]</sup>. Nitrogen-bases derivatives of  $\beta$ -diketone complexes are among the most widely studied coordination compounds because of their various applications as bactericides, fungicides<sup>[6-11]</sup>, precursors for Chemical Vapour Deposition (CVD) applications and thermal transfer printing materials<sup>[12-16]</sup>.

Metal complexes of  $\beta$ -Diketone have been studied and reported<sup>[17-20]</sup> but there is dearth information on the copper(II) complexes of 1,1,1-trifluoroacetylacetone with counter ions such as NO<sub>3</sub>, Cl and Br. Consequently, the aim is to study the physicochemical and the antimicrobial activities of mixed-ligand complexes of copper(II) with 1,1,1-trifluoroacetylacetone, 1,10-phenanthroline and 2,2'-bipyridine.

## 2. EXPERIMENTAL

### 2.1 Materials and Physical measurements

The following reagents were used: 1,1,1-trifluoroacetylacetone (Aldrich), copper nitrate hexahydrate, copper chloride, copper bromide, 2,2'-bipyridine and 1,10-phenanthroline (Analytical grade) were sourced commercially and used as supplied. The % metal in the mixed-ligand complexes were determined by titrimetric method with EDTA. The infrared spectra of the complexes, as pressed KBr disc, were recorded on the Buck 500 Scientific model infrared spectrophotometer in the region 4000-400 cm<sup>-1</sup>. The solution spectra of the complexes in methanol/chloroform were recorded on a Spectro UV-VIS double beam PC scanning spectrophotometer-UVD-2960. Magnetic susceptibilities were measured with a Sherwood Scientific magnetic susceptibility balance, MSB Mark 1.

### Synthesis of [Cu(TFA)(Phen)NO<sub>3</sub>]

1,1,1-trifluoroacetylacetone (0.5509mL) was added dropwisely into the stirring solution of copper nitrate trihydrate (1.0969g, 0.00454mol) dissolved in 2mL of distilled water. 1,10-phenanthroline (0.9g, 0.00454mol) was added and stirring continues for 1 hour. The precipitate was filtered and dried in the vacuo.

Yield: 21.26%,  $\mu_{\text{eff}} = 1.76\text{BM}$ . (Cal. Cu, 13.33; found Cu, 12.84), IR data for 1 (KBr, cm<sup>-1</sup>) 1627m, 1580m, 1518m, 1469w (C=O +C=C ring str), 1384vs (NO<sub>2</sub>str), 853s, 722s  $\nu$ (C-H)853-856 and 722-722 cm<sup>-1</sup>,

#### Synthesis of [Cu(TFA)(Bipy)NO<sub>3</sub>]

This complex was prepared with the following quantities: 1, 1, 1-trifluoroacetylacetone (0.5509mL), copper nitrate trihydrate (1.0969g, 0.00454mol), 2,2'-bipyridine (0.7091g, 0.00454mol) Yield: 13.99%,  $\mu_{\text{eff}} = 2.23\text{BM}$ . (Cal. Cu, 14.62; found Cu, 12.92), IR data for 2 (KBr, cm<sup>-1</sup>) 1623m, 1576m, 1518m, 1528w (C=O +C=C ring str), 1385w (NO<sub>2</sub> str), 770s  $\nu$ (C-H)

#### Synthesis of [Cu(TFA)(Phen)Cl]

This complex was prepared with the following quantities: 1, 1, 1-trifluoroacetylacetone (0.5509mL), copper chloride dihydrate (0.7740g, 0.00454mol), 1,10-phenanthroline (0.9g, 0.00454mol) Yield: 76.69%,  $\mu_{\text{eff}} = 2.02\text{BM}$ , (Cal. Cu, 13.50; found Cu, 14.11), IR data for 3 (KBr, cm<sup>-1</sup>) 1625m, 1584m, 1543\*, 1517s, (C=O +C=C ring str) 856s, 722vs  $\nu$ (C-H)

#### Synthesis of [Cu(TFA)(Phen)Br]

This complex was prepared with the following quantities: 1, 1, 1-trifluoroacetylacetone (0.5509mL), copper bromide (1.0141, 0.00454mol) in 50% methanol, 1, 10-phenanthroline (0.9g, 0.00454mol) Yield: 87.54%,  $\mu_{\text{eff}} = 2.2\text{BM}$ , (Cal. Cu, 12.84; found Cu, 13.53), IR data for 4 (KBr, cm<sup>-1</sup>) 1620m, 1583m, 1513m (C=O +C=C ring str), 854s, 721vs  $\nu$ (C-H)

#### Synthesis of [Cu(TFA)(Bipy)Br]

This complex was prepared with the following quantities: 1, 1, 1-trifluoroacetylacetone (0.5509mL), copper bromide (1.0141g, 0.00454mol) in 50% methanol, 2,2'-Bipyridine (0.7091g, 0.00454mol) Yield: 98.56%,  $\mu_{\text{eff}} = 1.87\text{BM}$ , (Cal. Cu, 14.04; found Cu, 13.88), IR data for 5 (KBr, cm<sup>-1</sup>) 1625vs, 1567w, 1526w, (C=O +C=C ring str), 771s  $\nu$ (C-H)

### Biological Studies

The antibacterial test was carried out at the Department of Pharmaceutical Microbiology, University of Ibadan, Ibadan, Nigeria.

#### 2.2 Antimicrobial Susceptibility Testing

The antimicrobial activity of the complexes prepared was determined by agar cup diffusion method using each compound in decreasing concentration of 200 mg/mL-6.25 mg/mL dissolved in methanol against isolated organisms. Plate cultures were prepared either by seeding (bacteria) or spreading using 0.1 mL of 10<sup>-2</sup> dilution from 12-18 hours. 3 drops of dissolved compound was used to fill each of the well dug in the set agar media; afterwards a pre-incubation diffusion period of 1 hour on bench was observed. Incubation of the cultured plates was observed at 37 °C for 24 hours. Observation of the plates for zones of growth inhibition, measured in mm was recorded [21].

### 3. RESULT AND DISCUSSION

Complexes have different shades of blue and green colours. All complexes melted within the range 143-269°C except [Cu(TFA)PhenNO<sub>3</sub>] whose melting point is above 300°C. The magnetic moments of copper(II) compounds are expected to be in excess of the spin-only ( $\mu_{\text{s.o}}$ ) value regardless of the stereochemistry, due to orbital contributions and 'mixing' of excited T terms into the ground terms [22].

The mixed-ligand complexes of copper(II) studied exhibit effective magnetic moment in the range 1.76 and 2.23 B.M. which fall in the range 1.7-2.2 B.M. normally observed for magnetically dilute compounds<sup>[20,22]</sup>.

The C=O +C=C ring str of the TFA-H occurred in the range 1786-1610cm<sup>-1</sup> as three distinct bands while C=O +C=C of the complexes occurred at 1625-1513cm<sup>-1</sup>. Lower frequency shifts of different magnitude were observed in the C=O +C=C vibrations of the complexes relative to TFA-H. NO<sub>2</sub>str bands occurred at 1384 and 1385 cm<sup>-1</sup> in [Cu(TFA)PhenNO<sub>3</sub>] and [Cu(TFA)BipyNO<sub>3</sub>] respectively. The CH deformation bands for the 1,10phenanthroline showed at 853-856 and 721-722 cm<sup>-1</sup> while that of bipyridine appeared at 770-771cm<sup>-1</sup>. The electronic spectra of the complexes were measured in methanol and chloroform. The results are presented in table 1. The visible spectra of complexes studied displayed a single broad band in the visible region with  $\lambda_{max}$  varying between 14,993-13,661 cm<sup>-1</sup> in chloroform which is consistent with square pyramidal geometry for copper (II) complexes<sup>[23]</sup>.

The increase in frequency on changing the solvent from methanol to chloroform further confirms that the complexes are square pyramidal in geometry.  $\pi_3-\pi^*_4$  were observed in the range 34,118-33,557cm<sup>-1</sup> in chloroform. [Cu(TFA)PhenNO<sub>3</sub>] and [Cu(TFA)PhenCl] showed pronounced activity on the tested bacteria (*Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*). All the mixed ligand copper(II) complexes showed moderate activity in *Pseudomonas aeruginosa*, *Salmonella enterica*, *Klebsiella pneumoniae* except [Cu(TFA)PhenCl] in *Pseudomonas aeruginosa* with pronounced activity. All the complexes were moderately active on the fungi strains tested except [Cu(TFA)PhenNO<sub>3</sub>] in *Candida albicans* and [Cu(TFA)PhenCl] in *Penicillium notatum*.

The TFA ligand showed pronounced activity in *Staphylococcus aureus* and *Bacillus subtilis* but were moderately active in *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella enterica*, and *Klebsiella pneumoniae*, [Cu(TFA)PhenNO<sub>3</sub>] and [Cu(TFA)PhenCl] had stronger activity on *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* than the standard drug used (gentamicin). The copper complexes exhibited moderate activity on the fungal strains used compared with Ketoconazole except [Cu(TFA)PhenNO<sub>3</sub>] and [Cu(TFA)PhenCl] which compared favourably well with Ketoconazole on *Candida albicans* and *Penicillium notatum* respectively.

#### 4. CONCLUSION

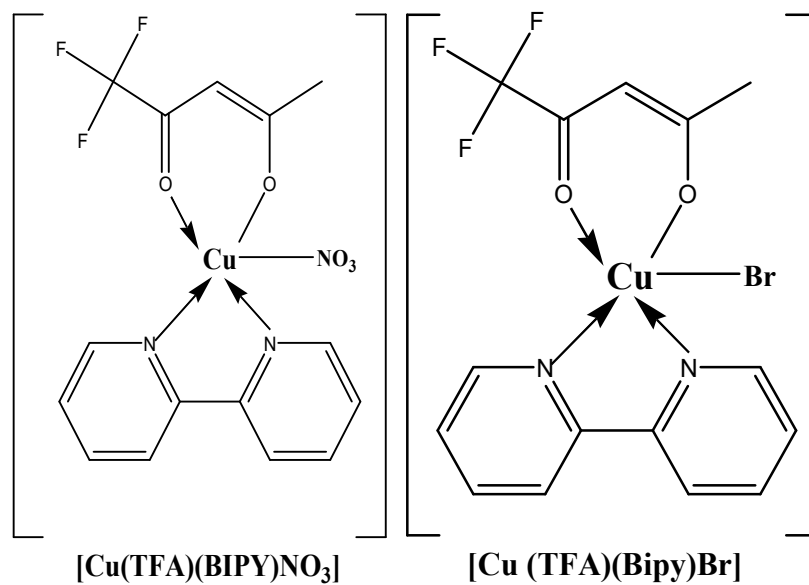
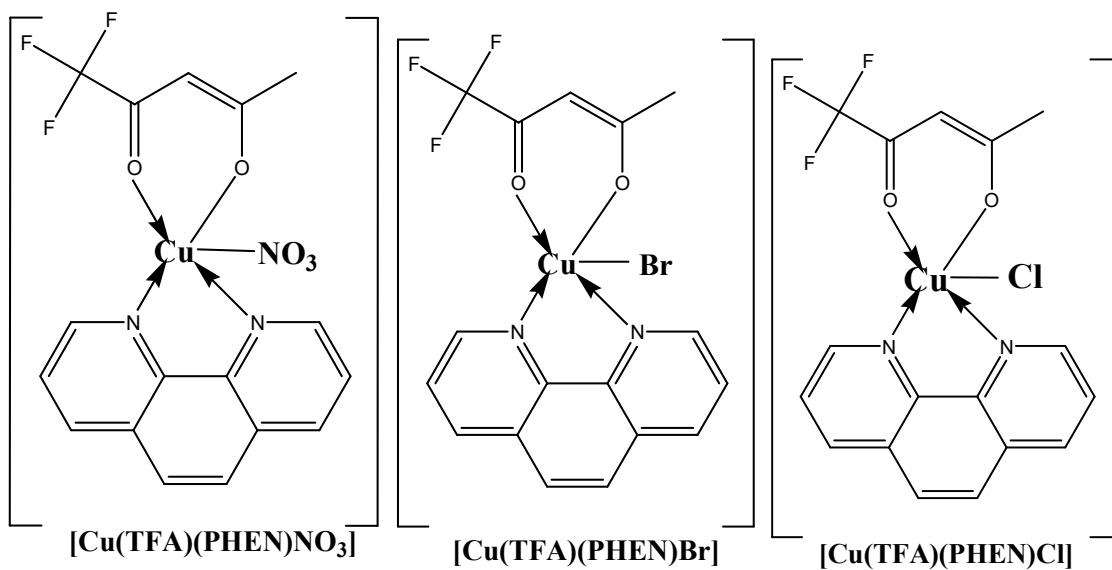
The copper complexes of 1,1,1-trifluoroacetylacetone with 1,10-phenanthroline and 2,2'-bipyridine have been synthesized. The copper(II) coordinated to two O-atoms present in 1,1,1-trifluoroacetylacetone, two N-atoms from 1,10-phenanthroline/2,2'-bipyridine and counter ion such as NO<sub>3</sub>, Cl and Br to give the proposed square pyramidal structure for all the complexes. With respect to antifungal activity, TFA and all the copper(II) complexes exhibited moderate activity in *Aspergillus niger* and *Rhizopus stolonifera* while the standard drug (ketoconazole) had stronger activity.

## REFERENCES

1. Agwara, M.O., Ndifon, N.B. and Mohamadou, A. (2010). Biological Activity of Organic Ligands and the Metals. *Bulletin of Chemical Society*, 24, 1-7.
2. Jian, L., Tingting, L., Sulan, C., Xin, W., Lei, I. and Yongmei, W. (2006). Synthesis, Structure and Biological Activity of Co(II) and Cu(II) Complexes of Valine-derived Schiff base. *International Journal of American Pharmaceutical Research*, 100, 1888-1896.
3. Li-June, M. (2003). Biological Activities of Complexes. *Medical Research Review*, 23,697-762.
4. Kawasaki, T., Osaka, Y. and Tsuchiya, T. (1980).4,5-disubstituted 2-(3,4,5-trimethoxyphenyl)-thiazoles and their Use in Pharmaceuticals or Treating Peptic Ulcers. *Ger. Offen.* 3, 026054, C.A. 95: 7265K.
5. Graddon, D.P. and Schulz, R.A. (1965). Adducts of Copper(II)  $\beta$ -diketone Chelates with Heterocyclic Bases. II. Chelates with 3-alkylacetylacetones. *Australian Journal of Chemistry*, 18, 1731-1742.
6. Teruaki, M., Toshiro, T., Tohru, Y. and Oliver, R. (1990). Nickel(II) Complex Catalyzed Epoxidation of Olefins with Molecular Oxygen and Primary Alcohol. *Chemistry Letters*, 9, 1661-4.
7. Bennett, I.J., Broom, R., Cassels, J., Elder, N.M. and Hanlon, J.(1999). Biological Properties of Organic Ligands. *Bioorganic and Medicinal chemistry Letters*, 9: 1847-1852.
8. Sato, K., Yamazoe, S., Yamamoto, R., Ohata, S. and Ando, A. (2008). Direct Synthesis of 1,3-Diketones by Rh- Catalyzed Reductive r-Acylation of Enones, *Organic letters*,10: 2405-2408.
9. Andrae, I., Bringham A., Bohm F., Gonzenbach H., Hill T., Mulroy L. and Truscott T.(1997). A UVA filter (4-tert-butyl-4'-methoxydibenzoylmethane): Photoprotection Reflects Photophysical Properties, *Journal of Photochemistry and Photobiology*, 37:147-150.
10. Omoregie, H.O., Obi-Egbedi, N. and Woods, J.A.O. (2014). Synthesis, Spectroscopic Properties and Structural Studies of Copper(II) Complexes of 2-Substituted-1,3-Diphenyl-1,3-Propanedione, Their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts. *International Journal of Chemistry*, Vol. 6(1), 71-76.
11. Omoregie, H. Oluwatola (2014). Physicochemical and Antimicrobial Properties of Cobalt(II) and Copper(II) Complexes with Nitrogen-containing Ligands. *Science Focus*, Vol. 19 (1), 52- 64.
12. Miura, N., Komamura, T., Abe, T. (1993). Metal ion sources for dye diffusion thermal transfer printing. *Hard Copy*,93, 314-317.
13. Troyanov, S.I., Kazima, N.P., Soboleva, I.E. and Chugarov, N.V. (1997). Packing in Crystal Structures of Metal  $\beta$ -diketonates used in MOCVD and its Correlation to Volatility. *Proceedings of Electrochemical Society*, 5, 886-892.
14. Hubert-Pfalzgraf, L.G. and Guillon, H. (1998). Trends in Precursor Design for Conventional and Aerosol-assisted CVD of High-Te Superconductors. *Applied Organometallic Chemistry*, 12, 221-236.

15. Lin, W., Wiegand, B.C., Nuzzo, R.G. and Girolami, G.S. (1996). Mechanistic Studies of Palladium Thin Film Growth from Palladium(II)  $\beta$ -diketonates. 1. Spectroscopic Studies of the Reactions of Bis(hexafluoroacetonato) palladium(II) on Copper Surfaces. *Journal of American Chemical Society*, 118, 5977-5987.
16. Banger, K.K., Ngo, S.C., Higashiya, S., Claessen, R.U., Bousman, K.S., Lim, P.N., Toscano, P.J. and Welch, J.T. (2003). Facile Synthesis of a Novel Class of Organometalloid-containing Ligands, the Sila-SS-diketones: Preparation, Physical and Structural Characterisation of the Copper(II) Complexes. *Journal of Organometallic Chemistry*, 67(1), 15-32.
17. Omoregie, H.O., Ibukun, D. T., and Adeleke, O.E. (2018). Synthesis, Characterization and Antimicrobial Activities of Mixed Ligand Copper(II) Complexes of 2,4-Pentanedione, 1,1,1-Trifluoro-2,4-Pentanedione, 1-Phenyl-1,3-Butanedione and their Adducts. *Archives of Applied Science Research* Vol. 10. No. 3: 1-9.
18. H.O Omoregie (2012). Synthesis, characterization and antimicrobial activities of Cobalt(II), Nickel(II) and Copper(II) Complexes of Benzoyltrifluoroacetone and their Adducts. *Science Focus* 17 269 – 278.
19. Woods, J.A.O., Omoregie, H.O., Retta, N., Chebude, Y., and Capitelli, F. (2009). Synthesis and Physicochemical Studies of Nickel(II) Complexes of 2-substituted-1,3-diphenyl-1,3-propanedione, their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts and X-Ray Structure of (2,2'-Bipyridine)Bis(1,3-diphenyl-1,3-propanedionato)Nickel(II). *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* Vol. 39. No. 10: 69.
20. Woods, J.A.O., Omoregie, H.O., Retta, N., and Capitelli, F. and Da Silva, I. (2009). Synthesis and Characterization of Some Nickel(II) and Copper(II) Complexes of 2-substituted-4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (TTAH), their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts and X-Ray Structure of (2,2'-Bipyridine) Bis(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato) Nickel(II). *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* Vol.39. No.10: 704-717.
21. H. Oluwatola Omoregie, P. Ojattah, O. E. Adeleke, J. A. O. Woods and F. Capitelli (2015). Synthesis, spectral, and antimicrobial studies of Nickel(II) complexes with Nitrogen-Containing Ligands. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 45.4 469-476.
22. Greenwood, N.N. and Earnshaw, A. 1997. *Chemistry of the elements. 2<sup>nd</sup> ed. Butterworths and Heinemann. pp1193.*
23. O.A. Odunola, M.A. Oladipo, J.A.O. Woods and A.C. Gelebe (2003). Synthesis and Structural Studies of Some Ternary Copper(II) Complexes Containing  $\beta$ -Diketones with 1,10-Phenanthroline and 2,2'-Bipyridyl and X-Ray Structure of  $[\text{Cu}(\text{C}_6\text{H}_5\text{COCHCOCH}_3)(\text{bipy})\text{Cl}]$ . *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* 33.5 857-871.

### APPENDICES - PROPOSED STRUCTURES



**Table 1. The assignments of the electronic solution spectra of the mixed ligand copper(II) complexes with 1,1,1-trifluoroacetylacetone and nitrogen containing ligands in methanol and chloroform.**

[Cu(TFA)phenCl]	[Cu(TFA)bipyNO <sub>3</sub> ]	[Cu(TFA)phen(NO <sub>3</sub> )]	[Cu(TFA)bipyBr]	[Cu(TFA)phenBr]	Tentative arrangement
<b>Methanol</b>					Benzoidband
44,643				44,444	$\delta_L-3d\delta_y/ \pi_3-$
36,630		36,630		36,630	$\pi_4$ bipy-phen
31,598	33,445 32,236	33,898	33,557 32,131	34,130	$\pi_3-\pi_4$
15,083	16,155	14,925	15,015	15,385	d-d
<b>Chloroform</b>					Benzoid
37,175	42,194 38,483	36,496		36,630	band/ $\delta_L-$
34,119	33,223	33,735	33,333	33,844	$\pi_3-\pi_4$
13,605	14,993	IS	14,164	13,661	d-d

**Table 2. Antimicrobial activity of TFAH and mixed ligand copper(II) complexes at 10mg/mL.**

	<i>S. aur</i>	<i>E. coli</i>	<i>B. sub</i>	<i>P. aer</i>	<i>S. typhi</i>	<i>K. pne</i>	<i>C.a</i>	<i>A.n</i>	<i>Pen</i>	<i>Rhiz</i>
TFA	20	18	20	18	14	14	16	16	14	14
[Cu(TFA)PhenNO <sub>3</sub> ]	24	26	26	20	18	18	20	18	18	18
[Cu(TFA)PhenCl]	20	24	24	18	16	18	18	16	20	16
[Cu(TFA)PhenBr]	26	18	18	14	14	14	16	16	14	14
[Cu(TFA)BipyBr]	16	18	14	14	14	16	14	14	16	14
[Cu(TFA)BipyNO <sub>3</sub> ]	18	16	18	16	14	14	16	18	16	14
Gentamicin(10mg/mL)	16	16	18	20	20	20	ND	ND	ND	ND
Ketoconazole	ND	ND	ND	ND	ND	ND	26	38	24	30
DMSO/Acetone	NO ACTIVITIES									

Zones of growth inhibition in millimeters (mm)

10-19=moderately active; 20-29=active; 30 and above=very active; R=organism resistant to the extract;

ND=not determined

*S. aur* = *Staphylococcus aureus*; *B. sub* = *Bacillus subtilis*; *K. pne* = *Klebsiella pneumonia*;

*E. coli* = *Escherichia coli*; *S. typhi*=*Serovar typhi*; *P. aer* = *Pseudomonas aeruginosa*;

*Ca* = *Candida albicans*; *An* = *Aspergillus niger*; *Pen* =*Penicillium notatum*; *Rhiz*=*Rhizopus stolonifer*

Tony Blair Institute for Global Change