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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

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ABSTRACT

Mixed ligand complexes of β-diketones of the form [Cu(tfa)(bzac)], [Cu(tfa)(acac)] and their 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts have been synthesized and characterized by metal analysis, electronic, infrared spectra and magnetic susceptibility measurements. Infrared spectra showed the shifting of bands at 1698 and 1588 cm^{-1} to lower frequency in the adducts. The d-d spectral band positions suggest square planar and octahedral geometries for the copper(II) complexes and their various adducts respectively. The magnetic moments of the copper(II) complexes and their various adducts suggest that they are magnetically dilute compounds. The copper(II) complexes exhibited broad spectrum of antimicrobial activity against the Gram-negative, Gram-positive and fungi tested generally at 100-25 mg/mL concentrations in-vitro. [Cu(tfa)(bzac)] was most outstanding in this regard.

Keywords: β-diketone, Mixed-ligand, Magnetochemistry, Spectra, Antimicrobial

INTRODUCTION

The wide applications of β-diketones have made it to be a ligand of choice in researches [1-7]. Metal β-diketonates have been reported to have potential pharmacological properties and are used as fuel additives and extraction purposes [8,9]. There is wide application of Metal β-diketonates in the industries and agriculture [10]. Literature has also revealed that metal β-diketonates are treated as aromatic systems because of the presence of benzenoid resonance in the chelate ring and they are used as catalysts and heat stabilizers in the industries [1,11]. Mixed ligand complexes containing β-diketones and nitrogen donors have been extensively studied over the years because of their peculiar spectroscopic, electrochemical, microbial features [12-15]. Various β-diketonate complexes and their adducts have been synthesized and characterized [16-23] but there is no report of the synthesis and characterization of mixed ligand complexes of β-diketones of the form [Cu(tfa)(bzac)], [Cu(tfa)(acac)] and their 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts. Hence we present our report on the synthesis, conductance, magnetic, spectra and biological properties of mixed ligand copper(II) complexes of 1,1,1-trifluoro-2,4-pentenedione, benzoylacetone, and acetylacetone and their 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts.

MATERIALS AND METHODS

1,1,1-trifluoro-2,4-pentenedione (tfa-H) benzoylacetone (bzac-H), acetylacetone (acac-H) (Aldrich chemicals), copper(II) acetate, 2,2′-bipyridine and 1,10-phenanthroline (Analytical grade). The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech). The magnetic susceptibilities at room temperature were measured using Sherwood magnetic susceptibility balance. The infrared spectra were measured using nujol on Perkin Elmer Spectrophotometer 11 FT-IR. The

electronic spectra of the compounds in methanol and chloroform were recorded on a Perkin Elmer Lambda double beam UV/VIS spectrophotometer using 1cm glass cell. The percentage metal in the copper(II) compounds were determined titrimetrically using EDTA.

Preparation of [Cu(tfa)(bzac)]

Copper acetate (0.89 g, 4.12 mmol) dissolved in 15 mL 60% methanol was added directly to a mixture of benzoylacetone (0.61g, 4.12 mmol) and 1,1,1-trifluoro-2,4-pentenedione (0.5 mL, 4.12 mmol) in 10 mL methanol. The reaction mixture was stirred at room temperature for 1 h. The grey solid product was collected by filtration, washed with water and methanol, and dried in vacuo.

Proposed Structures Of Complexes

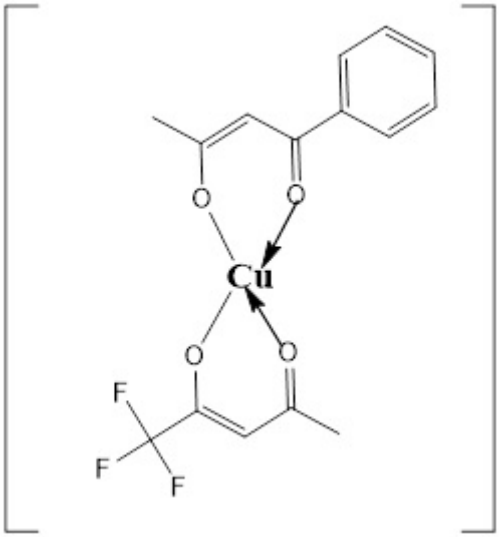

Figure 1: [Cu(tfa)(bzac)].

Preparation of [Cu(tfa)(bzac)(bipy)]

Copper acetate (0.89 g, 4.12 mmol) dissolved in 15 mL 60% methanol was added directly to a mixture of benzoylacetone (0.61 g, 4.12 mmol) and 1,1,1-trifluoro-2,4-pentenedione (0.5 mL, 4.12 mmol) in 10 mL methanol. The reaction mixture was stirred at room temperature for 30 minutes. 2,2'-bipyridine (0.64 g, 4.12 mmol) was added to the reaction mixture and stirred for 1 h. The green solid product was collected by filtration, washed with water and methanol, and dried in vacuo. Similar procedure was used for the preparation of the 1,10-phenanthroline adducts of the complex.

Proposed Structures Of Complexes

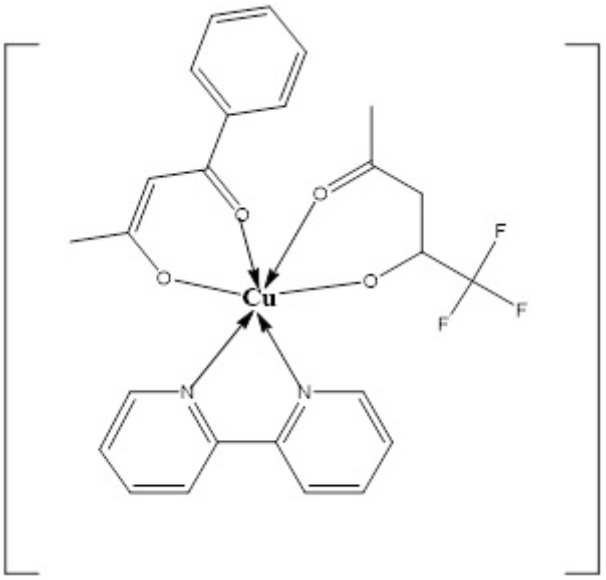

Figure 2: [Cu(tfa)(bzac)(bipy)].

Preparation of [Cu(tfa)(acac)]

Copper acetate (0.89 g, 4.12 mmol) dissolved in 15 mL 60% methanol was added directly to a mixture of 1,1,1-trifluoro-2,4-pentenedione (0.5 mL, 4.12 mmol) and acetylacetone (0.4 mL, 4.12 mmol) in 10 mL methanol. The reaction mixture was stirred at room temperature for 1 h. The grey solid product was collected by filtration, washed with water and methanol, and dried in vacuo.

Proposed Structures Of Complexes

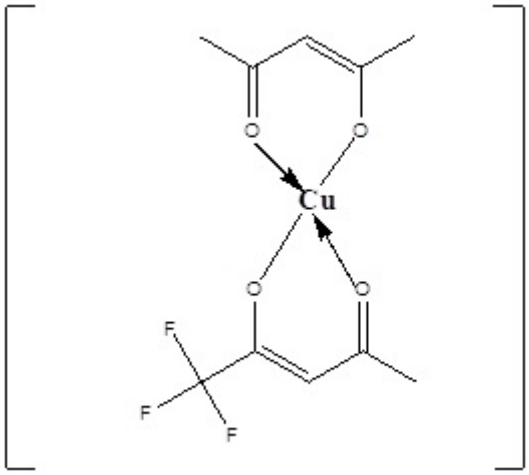

Figure 3: [Cu(tfa)(acac)].

Preparation of [Cu(tfa)(acac)(bipy)]

Copper acetate (0.89 g, 4.12 mmol)) dissolved in 15 mL 60% methanol was added directly to a mixture of acetylacetone (0.4 mL, 4.12mmol) and 1,1,1-trifluoro-2,4-pentenedione (0.5 mL, 4.12 mmol) in 10 mL methanol. The reaction mixture was stirred at room temperature for 30 minutes. 2,2'-bipyridine (0.64 g, 4.12 mmol) was added to the reaction mixture and stirred for 1 h. The green solid product was collected by filtration, washed with water and methanol, and dried in vacuo. Similar procedure was used for the preparation of the 1,10- phenanthroline adducts of the complex.

Proposed Structures Of Complexes

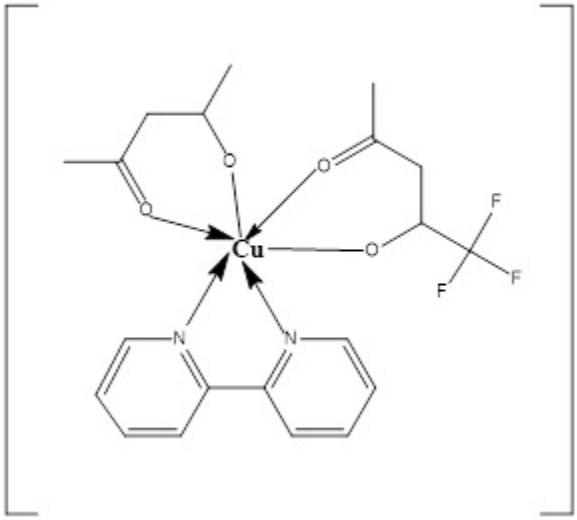

Figure 4: [Cu(tfa)(acac)(bipy)].

Microbiological studies

This study centred mainly on microbial susceptibility testing on selected laboratory clinical isolates of Escherichia coli, Klebsiella pneumonia, Staphylococcus aureus, Candida albicans and Penicillium notatum. Each of the copper complex was used against the respective isolates at 100, 50, 25, 12.5 and 6.25 mg/mL. This study was carried out at the Department of pharmaceutical microbiology, university of Ibadan, Nigeria where the microbial isolates were obtained.

ANTIMICROBIALS SCREENING

Methodology

The antimicrobial activity of the synthesized compounds was determined by agar cup diffusion method using each compound in decreasing concentration of 100-6.25 mg/mL dissolved in either sterile distilled water or methanol against every microbial isolate tested. Plate cultures were prepared either by seeding (bacterial and yeast) or spread plate (moulds) using 0.1mL of 10-2 dilution from 18 -12 h-old broth culture of each bacterium or 24 to 72 h old broth of each fungus, in nutrient agar (bacteria) and sabouraud dextrose agar (fungi). Each of the wells dug in the set agar medial was filled with three drops of the dissolved compound, 100 mg/mL followed by pre-incubation diffusion period of 1 h. on bench. The cultured plates were incubated at 37 °C for 24 h (bacteria) and 28 °C for 24-72 h (fungi). Thereafter, the antimicrobial susceptibility was assessed by observing the plates for zones of growth inhibition, measures in mm [24]. The results are presented in Table 4.

RESULTS AND DISCUSSION

Table 1: Analytical and physical data of copper(II) complexes of 2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 1-phenyl-1,3-butanedione and their adducts.

Compounds	Mol. wt. (g mol–1)	Colour	M.pt(oC)	%Metal Exp (Cal)	Yield%	μeff (B.M.)
Cu(tfa)(acac)]	315.73	Grey	254-256	20.13(20.06)	63.24	1.9
[Cu(tfa)(acac)(phen)]	495.93	Green	218-220	12.80(12.65)	45.04	1.83
[Cu(tfa)(acac)(bipy)]	475.91	Light green	>300	13.46(13.40)	36.13	1.86
[Cu(tfa)(bzac)]	377.81	Grey	257-259	13.60(13.40)	49.3	1.89
[Cu(tfa)(bzac)(phen)]	558.02	Light green	287-300	10.40(11.38)	69.7	-

[Cu(tfa)(bzac)(bipy)]	533.99	Light green	>300	11.90(11.87)	52.04	-

Table 1 shows the analytical data, colours, percentage yield and room temperature magnetic moments (μeff) of the prepared copper(II) complexes and adducts. The % metal analysis were in good agreement with those calculated for the proposed structure. The copper complexes were obtained as various shades of grey and green colours.

Table 2: Relevant infrared bands (cm^{-1}) of copper(II) complexes of 1,1,1-trifluoro-2,4-pentenedione, benzoylacetone, acetylacetone and their adducts.

Formula	vas(C=O)+vas(C=C)	ν(C-O)+δC-H	ν(C-H)Phen/bipy
tfa-H	1708s, 1609s		
bzac-H	1599m, 1540b		
acac-H	1713s, 1614s		
[Cu(tfa)(acac)]	1698w, 1576s	1491w, 1469w	
[Cu(tfa)(acac)(phen)]	1615, 1580	1453w, 1424w	856s, 721s
[Cu(tfa)(acac)(bipy)]	1601vs, 1565	1494, 1471	766vs
[Cu(tfa)(bzac)]	1588s, 1558s		
[Cu(tfa)(bzac)(phen)]	1583m	1470s	853s, 720s
[Cu(tfa)(bzac)(bipy)]	1566s	1470s	776vs

Table 3: Electronic solution spectra of copper(II) complexes of 1,1,1-trifluoro-2,4-pentenedione, acetylacetone and their adducts.

acac-H	tfa-H	[Cu(tfa)(acac)]	[Cu(tfa)(acac)phen]	Tentative Assignment
Methanol	49,510	41,322	44,843	π3−π5∗
49,510	44,640			
44,250				
35,710*	35,710	34,130	36,765,	π3−π4∗
34,010			34,130	
		15,528	15,015	d-d
Chloroform		41,152		σ_L-3dxy/p-p (bipy.phen)
36,500	35,460	33,670	36,630	π3−π∗4
			34,843	
			30,303	n-p*/p-d
		18,182	15,291	d-d
		15,152		

Table 4: Electronic solution spectra of copper(II) complexes of 1,1,1-trifluoro-2,4-pentenedione, benzoylaceton and their adducts

tfa-H	bzac-H	[Cu(tfa)(bzac)]	[Cu(tfa)(bzac)(phen)]	[(Cu(tfa)(bzac)(bipy)	Tentative Assignment
Methanol					
49510					π3−π5∗
44640			44843		

	40486	39526	36900	40486	Benzenoid band/σ_L-3d_{xy}/π-π (bipy.phen)
35710	32258	31446	33898	33445	π3−π4∗
				32154	
				30303	n-π*/π-d
		15504	14388	14327	d-d
Chloroform	43,860*	38610		38911	Benzenoid band/σ_L-3dxy/π-π (bipy.phen)
35460	32258	32154	36232	34602	π3−π∗4
		31153	33,784,	32258	
			32362		
		30303	30303	30303	n-π*/π-d
		19231	14993	14993	d-d
		15152			

Table 5: Antimicrobial activity data of diketone and the mixed Ligand copper(II) complexes of 1,1,1-trifluoro-2,4-pentenedione, benzoylacetone, acetylacetone and their adducts.
Growth inhibition zone in millimeters (mm) 10-19-Intermediate, 20-29-sensitive, 30 and above- v. sensitive, R= Resistant, S. aureus = Staphylococcus aureus, K. pne = Klebsiella pneumonia, E. coli = Escherichia coli, C.albicans = Candida albicans; A. niger = Aspergillus niger; P. notatum = Penicillium notatum, NA-not applicable G-Gentamicin T-Tioconazole.

Compound/ organism	**[Cu(tfa)(bzac)]**					**[Cu(tfa)(bzac)(phen)]**					**[Cu(tfa)(acac)(phen)]**					**G**	**T**
	(mm)					(mm)					(mm)					10	70%
	100	50	25	13	6.25	100	50	25	12.5	6.25	100	50	25	12.5	6.25		
	(mg/mL)					(mg/mL)					(mg/mL)						
S. aureus	16	15	20	15	R	13	13	15	13	13	25	19	15	12	R	38	NA
K. pneumonia,	28	28	24	21	18	19	19	15	16	19	25	18	13	10	R	40	NA
E. coli	30	26	26	20	13	25	25	25	25	25	25	20	17	15	R	38	NA
C. albicans	20	20	15	R	R	16	16	15	10	R	28	20	20	16	10	NA	28
P. notatum	30	30	20	19	20	20	20	20	15	R	22	18	20	20	16	NA	28
A. niger	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	NA	28
Methanol	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R

Magnetic moment

The magnetic moment data as shown in Table 1 depicts the paramagnetic nature of the compounds. Our synthesized copper(II) complexes and adducts had magnetic moment in the range 1.83- 1.90 B.M. which falls in the range for magnetically dilute copper(II) compounds [21].

Infrared spectra

The principal IR absorption bands of the prepared complexes are listed in Table 2. In the spectrum of the ligand, the band observed around 1713 cm^{-1} and 1614 cm^{-1} have been assigned as ν_{as}(C=O)+ν_{as}(C=C) vibrations. Upon complexation, lower frequency shifts of the ν_{as}(C=O)+ν_{as}(C=C) stretching vibration was observed in [Cu(tfa)(acac)] and [Cu(tfa)(bzac)] showing the coordination of the ligand to the metal through the oxygen atom of the ligands. Lower frequency shifts were also observed in the adducts relative to the metal complexes with the [Cu(tfa)(bzac)(bipy)] and [Cu(tfa)(acac)(bipy)] having the lowest shifts. The bands at 766 and 756 cm^{-1} in bipyridine adducts have

been assigned as C-H deformation bands while in phenanthroline adducts the deformation bands occurred at the region 856 cm^{-1} and 720cm^{-1}[17, 25, 26].

Electronic spectra

The electronic spectra of the ligands, the complexes and their adducts in chloroform and methanol are listed in Table 3. Bands in the 1,1,1-trifluoro-2,4-pentenedione observed at 35,710-35,460 cm^{-1}in methanol/chloroform have been assigned to the π3-π4* transition band. The π3-π4* transition band of the benzoylacetone was observed at 32,258 cm^{-1} in both chloroform and methanol while the Benzenoid band was observed at 40,486 cm^{-1} and 43,860* cm^{-1} in methanol and chloroform respectively [17,27,28]. Bathochromic shifts of the π3-π4* transition band were observed in the synthesized copper complexes in both methanol and chloroform relative to the observed band in ligand spectra while hypsochromic shifts were observed in the adducts relative to the complexes. Square planar Cu(II) commonly shows a broad band between 13000 -20000 cm^{-1} and a little shoulder between 18000-21000 cm^{-1}. The synthesized [Cu(tfa)(acac)] had a broad band at 15,152 cm^{-1} and a little shoulder at 18,519 cm^{-1} in chloroform, this indicate a probable four coordinate square planar geometry. The [Cu(tfa)(bzac)] also shows a probable four coordinate square planar geometry with a broad band at 15,152 cm^{-1} and a shoulder at 19,231 cm^{-1} in chloroform [24]. In the visible spectra of the synthesized copper(II) adducts, a single broad band between 14,327-15,291 cm^{-1} were observed in both methanol and chloroform. Three transitions are expected for tetragonal distorted copper(II) complex but these bands overlap to form a broad band around 11000-16000 cm^{-1} [12,29]. The broad band observed in the synthesized Copper (II) adducts showed broad bands in the 14,327 to 15,015 cm^{-1} region indicating a probable octahedral geometry. Literature has also shown that the d-d absorption band position of copper with six-coordinate octahedral geometry remains unchanged in both coordinating (methanol) and non-coordinating solvents (chloroform) [29,30]. The close proximity of the d-d absorption bands of our synthesized adducts in methanol and chloroform indicates that all the adducts are octahedral in geometry.

Antimicrobial activities

The graded concentrations, 100-25 mg/mL of the copper complex and adducts were inhibitory generally against both the bacterial and fungal isolates tested, suggesting a broad spectrum of antimicrobial activity for [Cu(tfa)(bzac)], [Cu(tfa)(bzac)(phen)] and [Cu(tfa)(acac)(phen)]. The broad spectrum of activity was most pronounced with [Cu(tfa)(bzac)] with respect to the bacterial isolates. It is remarkable that the [Cu(tfa)(bzac)] and [Cu(tfa)(bzac)(phen)], considering the zones of growth inhibition recorded, were more inhibitory on Escherichia coli and Klebsiella pneumoniae (Gram-negatives) than Staphylococcus aureus (Gram-positive). Moreover, against Klebsiella pneumoniae and Staphylococcus aureus the control standard drug, gentamicin was virtually not inhibitory but against Escherichia coli, both the complexes and gentamicin at 10µg/mL compared favourably with each other. The control standard Ticonazole and the three complex and adducts compared also favourably well in their activities.

CONCLUSION

Six new complexes and adducts have been synthesized and characterized. A probable square planar and octahedral geometry have been suggested for the mixed ligand copper(II) complexes and their 1,10-phenanthroline and 2,2'-bipyridine adducts respectively. The antimicrobial inhibitory activity obtained for [Cu(tfa)(bzac)], [Cu(tfa)(bzac)(phen)], and [Cu(tfa)(acac)(phen)] could suggest them for use on inanimate materials, that is, as disinfectants.

REFERENCE

1. Shubhankar Kumar Bose, et al, **2016**. Highly Efficient Synthesis of Alkylboronate Esters via Cu(II)-Catalyzed Borylation of Unactivated Alkyl Bromides and Chlorides in Air. *Am Chem Soc Cat*, 6; p.8332−8335.
2. Kljun J, et al, **2017**. β-diketones as Scaffolds for Anticancer Drug Design -From Organic Building Blocks to Natural Products and Metallodrug Components, *Eur J Chem*, p.1655–1666.
3. Malekshah R E, et al, **2017**. Crystal structure, molecular docking and biological activity of the zinc complexes with 2-thenoyltrifluoroacetone and N-donor heterocyclic ligands. *J Mol Struct,* 1150; p.155–165.
4. Schwieger S, et al, **2009**. Platina-β-diketones as catalysts for hydrosilylation and their reactivity towards hydrosilanes. *J Organomet Chem*, 694(22); p. 3548-3558.
5. Xingbang H, et al, **2009**. Acetylacetone–Fe catalyst modified by imidazole ionic compound and its application in aerobic oxidation of β-isophorone. *Catal Commun*, 10(14); p.25.
6. Ferreira LC, et al, **2002**. *Polymer*, 43(14); p.3857-3862.

7. Wanninger S, et al, **2015**. Metal complexes of curcumin- synthetic strategies, structures and medicinal applications. *Chem Soc Rev*, 44; p. 4986–5002.
8. Onawumi OOE, et al, **2008**. Synthesis, structure and spectral studies on mixed ligand copper(II) complexes of diimines and acetylacetonate. *Polyhedron*, 27; p. 113-117.
9. Wenzel TJ, et al, **1985**. Studies of metal chelates with the novel ligand 2,2,7-trimethyl-3,5-octanedione. *Polyhedron*, 4(3); p. 369-378.
10. Hiroshi F, et al, **1987**. Toner for development of electrostatic images. *Chem Abstracts*, 106; 205178t.
11. Akangbe FA, et al, **1998**. The antimicrobial activities of the nickel(II) amd copper(II) complexes of various β-diketones and their adducts. *Biosci Res commun*, 10(4); p.317-322.
12. Odunola O A, et al, **2003**. Synthesis and structural studies of some ternary copper(II) complexes containing β-diketones with 1,10-phenanthroline and 2,2'-bipyridyl and x-ray structure of Cu(C6H5COCHCOCH3) (bipy)Cl . *Synth React Inorg Met-Org Chem*, 33(5); p. 857-871.
13. Meyer M, et al, **1999**. Stacking-induced cooperativity in copper(I) complexes with phenanthroline ligands. *Inorg Chem*, 38; p. 2279-2287.
14. Omoregie HO, et al, **2016**. Synthesis, characterisation and antimicrobial studies of nickel(II) mixed ligand complexes of β-diketones with nitrogen-containing ligands. *J Sci Res*, 15; p. 88-94.
15. Omoregie HO, et al, **2018**. Synthesis, characterisation and antimicrobial activities of cobalt(II) and copper(II) complexes of 4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedione and their Adducts. *Nig J Sci*, (IN PRESS).
16. Woods JAO, et al, **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). *Synth React Inorg Met-Org, Nano-Met Chem*, 39 (10); p. 69.
17. Woods JAO, et al, **2009**. Synthesis and Characterization of Some nickel(lI) 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). *Synth React Inorg Met-Org, Nano-Met Chem*, 3910; p. 704-717.
18. Omoregie H Oluwatola, et al, **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. *Int J Chem*, 6; p.1 71.
19. Omoregie O, et al, **2011**. Synthesis and Physicochemical Studies of Some 2-substituted-1-phenyl-1,3-butanedionato Nickel(II) and Copper(II) Complexes and their 2,2′-Bipyridine and 1,10-Phenanthroline Adducts. *Int J Chem*, 3(1); p.207-215.
20. Patel KS, et al, **1990**. Preparation and physico-chemical studies of some 3-substituted-2,4-pentanedionato copper(II) complexes and their adducts. *Synth React Inorg Met-Org Chem*, 20(1);97-109.
21. Omoregie, **2012**. Synthesis, characterization and antimicrobial activities of cobalt(II), nickel(II) and copper(II) complexes of benzoyltrifluoroacetone and their adducts. *Sci focus*, 17(3); p. 269-278.
22. Omoregie H Oluwatola, **2014**. Physicochemical and antimicrobial properties of Cobalt(II) and Copper(II) complexes with nitrogen-containing ligands. *Sci focus*, 19 (1); p. 52- 64.
23. Lever AB, **1984**. *Inorg Electron spectr.*
24. Omoregie HO, et al, **2014**. Synthesis, Spectral, and Antimicrobial Studies of Nickel (II) Complexes with Nitrogen-Containing Ligands, Synthesis and Reactivity in Inorganic. *Met-Org, Nano-Met Chem*, 45(4), p. 469-476.
25. Oladipo Mary Adelaide, et al, **2013**, Synthesis, Spectroscopic Characterization and Theoretical Studies of Copper (II) 1, 3-Diphenylpropane-1, 3-Dione Complex and its 1, 10-Phenanthroline, 2, 2-Bipyridine Adducts. *Int J Pure Appl Sci Technol*, 17(1), p. 1-10.
26. Ogden D, et al, **2013**. Ultraviolet spectra studies of β -ketoenolate complexes of oxovanadium (IV). *J Inorg Nucl Chem*, 30; p.1227-1236.
27. Patel KS, et al, **1979**. Physicochemical studies of metal β -diketonate-V. Spectral and magnetic properties of the Al(III), Cr(III), Mn(III), Fe(III) and Co(III) complexes of 1-(2-thienyl)-1,3-butanedione and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. *J Inorg Nucl Chem*, 42; p. 1241-1246.
28. Omoregie HO, et al, **2010**. Physicochemical studies of copper(II) β-diketonate: Magnetic and spectral properties of copper(II) complexes of 2-alkyl-1-phenyl-1,3-butanedione, their 2,2′-bipyridine and 1,10-phenanthroline adducts. *Arch. Appl. Sci. Res*, 2 (4): p. 7-16.

29. Patel KS, et al, **1990**. Synthesis and physico-chemical properties of Bis(3-akyl-2,4-pentanedionato) copper(II) complexes and their adducts with 2,2'-bipyridine and 1,10-phenanthroline. *Synth React Inorg Met-Org Chem*, 20(7); p. 909-922.