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SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITIES OF MIXED LIGAND NICKEL(II),COPPER(II) AND ZINC(II) COMPLEXES OF BENZALDEHYDE WITH 1,10-PHENANTHROLINE, 2,2′-BIPYRIDINE AND ETHYLENEDIAMINE

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ABSTRACT

Nickel(II), copper(II) and zinc(II) mixed ligand complexes of benzaldehyde with 1,10-phenanthroline, 2,2′-bipyridine and ethylenediamine have been synthesised and characterised by metal analysis, infrared spectroscopy, electronic spectra studies, magnetic susceptibility measurement and antimicrobial activities. The infrared spectra of the complexes confirmed the coordination through the carbonyl oxygen of the benzaldehyde while the electronic transitions are consistent with the adoption of octahedral geometry for all the synthesised complexes. The magnetic moment of the synthesised complexes suggested that all the complexes were paramagnetic except Zn(II) complex which was diamagnetic. The microbial susceptibility testing showed that the copper complexes had stronger antibacterial and antifungal activity than nickel and zinc complexes. Notably, $[Cu(Bz)_2Bipy(NO_3)_2]$ and $[Ni(Bz)_2(phen)Cl_2].H_2O$ showed no antifungal activity.

Keywords: Benzaldehyde, Mixed-ligand, Spectroscopy, Magnetochemistry, antimicrobial.

1. Introduction

Benzaldehyde as one of the important aromatic aldehydes, has wide uses and applications in many fields. Benzaldehyde was used as intermediate for aromatic alcohols, solvents for oils, resin, cellulose acetate and nitrate, manufacture of benzoic acid, pharmaceuticals and synthesis of Schiff bases (Durrant, 1961; EPA, 2003). A great deal of literature is available on metal complexes of Schiff base prepared from benzaldehyde. In recent times, transition metal complexes of benzaldehyde schiff base ligand have attracted considerable attention, not only due to their spectroscopy properties and application but due to their remarkable antibacterial, antitumor and antifungal properties (Spange *et al.*, 1999; Tumer *et al.*, 1999).

Studies have reported metal complexes prepared from benzaldehyde Schiff base but there is dearth of information on mixed ligand metal(II) complexes of benzaldehyde with 1,10-phenanthroline, 2,2′-bipyridine and ethylenediamine. Hence this suggests the need to synthesise these complexes and characterise them using physical methods such as infrared and electronic spectroscopy, magnetic susceptibility measurement and biological properties.

2. Materials and methods

Reagents and solvents

These include benzaldehyde, 1,10-Phenanthroline, ethylenediamine and 2,2′-bipyridine, copper nitrate trihydrate, nickel chloride hexahydrate, zinc nitrate hexahydrate, methanol, acetone and chloroform. They are of analytical grade were utilized without further purification.

Preparation of $[Cu(Bz)_2Bipy(NO_3)_2]$

Benzaldehyde (0.283 mL, 2.775 mmol) was added dropwisely into 2,2′–bipypridine (0.4334 g, 2.775 mmol) dissolved in 5 mL methanol while stirring; copper (II) nitrate trihydrate (0.6704 g, 2.775mmol) was then added into the solution. The resulting mixture was stirred for an hour and the complex formed was filtered, washed with methanol and dried. Similar procedure was used for the preparation of the phenanthroline and ethylenediamine complexes.

Preparation of $[Ni(Bz)_2BipyCl_2]$ (1:1:1)

Benzaldehyde (0.283 mL, 2.775 mmol) was added dropwisely into 2,2′-bipypridine (0.4334 g, 2.775 mmol) dissolved in 5mL methanol while stirring; nickel chloride (0.659 g, 2.775 mmol) dissolved in water was then added into the solution. The resulting mixture was stirred for an hour and the complex formed was filtered, washed with methanol and dried. Similar procedure was used for the preparation of the phenanthroline complex.

Preparation of $[Zn(Bz)_2(en)(NO_3)_2]$.$6H_2O$ (1:1:1)
Benzaldehyde (0.283 mL, 2.775 mmol) was added drop wisely into ethylenediamine (0.185 mL, 2.775 mmol) dissolved in 5mL methanol while stirring zinc nitrate hexahydrate (0.283 g, 2.775 mmol) was then added into the solution. The resulting mixture was stirred for an hour and the complex formed was filtered, washed with methanol and dried.

Physical Measurement
The percentage metal was determined using a titrimetric method while IR Spectra were recorded in the range 4000-400 cm^{-1} using nujol on Perkin Elmer 11 FT-IR Spectrometer. UV-V is spectra of the samples were measured in the range 190-900 cm^{-1} using a Perkin Elmer Lambda 950 UV-Vis Spectrophotometer. The magnetic susceptibility of the samples was measured with a Sherwood Scientific Magnetic susceptibility balance, MSB Mark1. Melting Points of the compounds were determined using a Gallenkamp melting point Apparatus, at the Department of Chemistry, University of Ibadan, Nigeria.

4. Result and discussion
The colour, melting point and percentage yield are presented in Table 1. The melting point of the complexes range from 198-281^oC, except that of $[Ni(bz)_2(bipy)Cl_2]$ and $[Zn(bz)_2(en)(NO_3)_2]$ which were greater than 300^oC, indicating high thermal stability for the complexes. All the complexes were soluble in DMSO and methanol except $[Cu(Bz)_2(phen)(NO_3)_2].6H_2O$, only Ni(II) complexes were soluble in chloroform while the rest were insoluble.

Table1: Analytical and physical data of nickel(II), copper(II) and zinc(II) complexes of benzaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine

Compounds	Mol. wt. ($gmol^{-1}$)	Colour	M.pt(^oC)	%Metal Exp (Cal)	Yield%	μ_{eff} (BM)
$[Cu(bz)_2(bipy)(NO_3)_2]$	555.99	Light blue	281-283	11.40(11.63)	8.27	1.72
$[Cu(bz)_2(en)(NO_3)_2].3H_2O$	503.20	Purple	246-248	12.60(12.30)	18.20	2.40
$[Cu(bz)_2(phen)(NO_3)_2].6H_2O$	687.95	Green	296-298	9.20(9.00)	30.00	1.84
$[Ni(bz)_2(phen)Cl_2].H_2O$	540.07	Pink	198-200	10.90(11.00)	16.90	2.60
$[Ni(bz)_2(bipy)Cl_2]$	498.12	Green	>300	11.70(11.00)	41.30	3.80
$[Zn(bz)_2(en)(NO_3)_2].6H_2O$	569.72	Pink	>300	11.47(11.50)	6.90	0.00

Magnetic moments
The room temperature magnetic moments for the complexes are presented in table 1. Octahedral nickel complexes usually have moment in the range 2.80 – 3.40 B.M while tetrahedral complexes have values in the range of 3.2 - 4.2. Literature has shown that unusual moment of 2.97 and 3.78 B.M. have been reported for tetrahedral and octahedral nickel (II) complexes respectively (Patel and Woods, 1999). The synthesised nickel(II) compounds had values within the range of 2.60-3.80 B.M. The magnetic moment for $[Ni(Bz)_2phenCl_2].H_2O$ was 2.60 B.M. which is lower than expected, this may be due to interconversion of stereochemistries and/or dimerization (Osowole *et al*., 2000). The synthesised copper (II) complexes had moments in the range 1.72-2.4 B.M. which is in agreement with the range expected for magnetically dilute compounds and are not subject to intermolecular magnetic interactions. $[Cu(Bz)_2(en)(NO_3)_2].3H_2O$ has magnetic moment of 2.4 B.M. which indicates that there is considerable orbital contribution at room temperature (Sunkari *et al*., 2015; Lawrence *et al*., 1999; Chandra and Gupta, 2009). The synthesised zinc complex has a magnetic moment of zero, which is in agreement with value expected for diamagnetic metal. (Sunkari *et al*., 2015).

Infrared spectra
The relevant infrared spectra of the complexes are listed in Table 3. The IR spectra of Benzaldehyde showed *ν*(C=O) absorption band at 1703 and 1653 cm^{-1}. There was a bathochromic shift of these bands to lower wave numbers in all the complexes in the range of 1564 – 1628 cm^{-1}, these is an indication that the benzaldehyde was coordinated through the carbonyl oxygen. Vibrations observed at 1519 – 1564 cm^{-1} was assigned to *ν*(C=N) of the 1,10-phennathroline and 2,2′-bipyridine. The shifting towards lower frequency due to the contribution of the nitrogen to the coordination (Amer *et al*., 2017; Kartha and Patho, 1967).

Table 3. Relevant infrared data of mixed ligand nickel(II), copper(II) and zinc(II) complexes of benzaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine

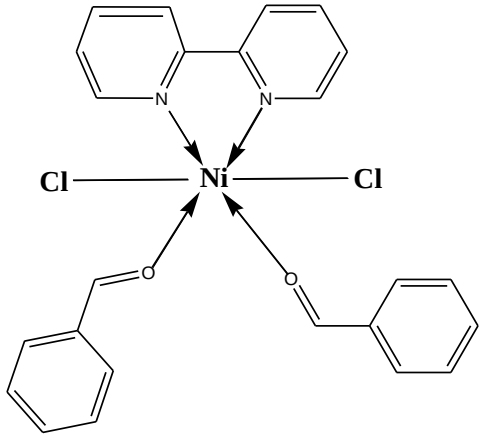
Compound	ν(C=O)	ν(C=N)	ν(M-N)	ν(M–O)
Bz	1703s, 1653s	-	-	
$[Cu(bz)_2(bipy)(NO_3)_2]$	1600w	1564s	470w	649w
$[Cu(bz)_2(en)(NO_3)_2].3H_2O$	1604m	-	413w	637s
$[Cu(bz)_2(phen)(NO_3)_2].6H_2O$	1628w	1519w	386w	649w
$[Ni(bz)_2(phen)Cl_2].H_2O$	1625m	1585s	484m	641w
$[Ni(bz)_2(bipy)Cl_2]$	1602s	1563s	477s	687m
$[Zn(bz)_2(en)(NO_3)_2].6H_2O$	1603s		464m	667w

Electronic spectra

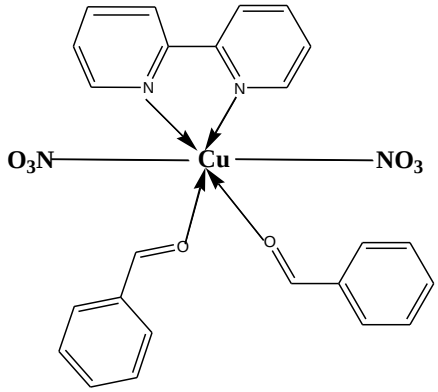
The results of the electronic solution spectra of the complexes in methanol and solid reflectance in nujol are shown in table 4 and 5 respectively. The electronic solid reflectance spectra showed bands at 32,087 – 33,783 cm^{-1} and 39,505 - 39,682 cm^{-1} which are assigned to the π-π* and charge transfer transitions respectively (Omoregie *et al.*, 2013, Amer *et al.*, 2017).

The electronic spectra of $[Ni(Bz)_2(phen)Cl_2].H_2O$ and [Ni(Bz)(Bipy)Cl] showed distinct single band at 14,925 cm^{-1} and 18,518 cm^{-1} respectively which has been assigned as a $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition in octahedral geometry. Amer *et al.*, 2017; Lever, 1982). $[Cu(Bz)_2Bipy(NO_3)_2]$, $[Cu(Bz)_2(en)(NO_3)_2].3H_2O$ and $[Cu(Bz)_2(phen)(NO_3)_2].6H_2O$ showed a d-d single broad band absorption around 13,140 – 18,148cm^{-1} which has been assigned as octahedral geometry. The spectrum of $[Zn(Bz)_2(en)(NO_3)_2].6H_2O$ complex exhibited a strong intense charge transition (LMTC) band at 20,366cm^{-1} (Rajesh *et al.*, 2006).

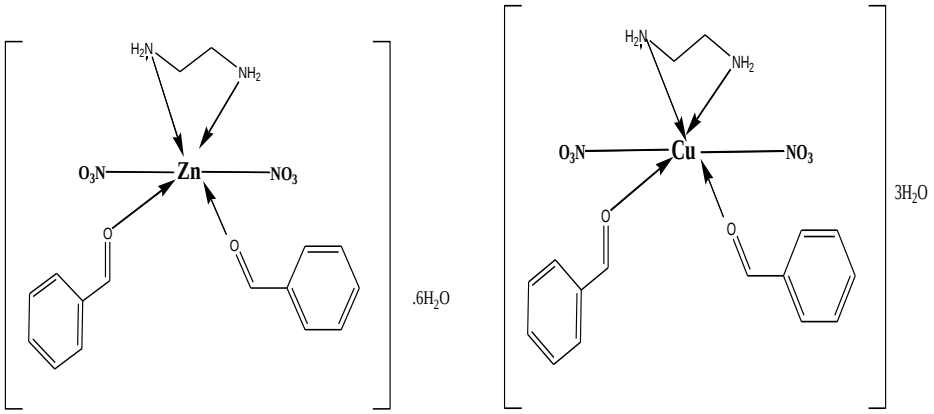
The electronic spectral data in methanol showed bands between 32,679 – 37,313 cm^{-1} with additional band observed between 40,983 – 44,642 cm^{-1} which has been assigned to π→π* and charge transfer transitions respectively. The bands in the visible region also showed that the prepared complexes are of octahedral geometry.



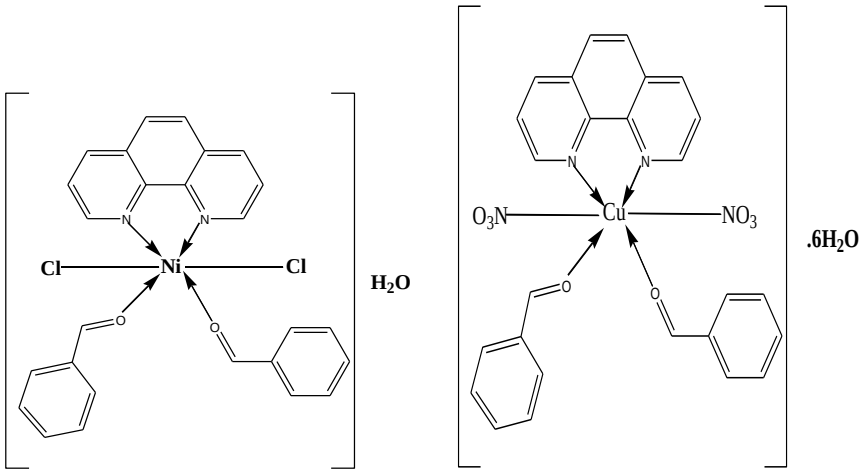
$[Ni(bz)_2(bipy)(Cl_2)]$



$[Cu(bz)_2(bipy)(NO_3)_2]$



$[Zn(bz)_2(en)(NO_3)_2].6H_2O$ $[Cu(bz)_2(en)(NO_3)_2].3H_2O$



$[Ni(bz)_2(phen)(Cl_2)].H_2O$ $[Cu(bz)_2(phen)(NO_3)_2].6H_2O$

Table 4. The electronic spectral data of mixed ligand nickel(II), copper(II) and zinc(II)complexes of benzaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine in methanol.

S/N	Compounds	π-π*/charge transfer transition	d-d transition
1	$[Cu(bz)_2(bipy)(NO_3)_2]$	33783, 42372	13888
2	$[Cu(bz)_2(en)(NO_3)_2].3H_2O$	46943	18248
3	$[Cu(bz)_2(phen)(NO_3)_2].6H_2O$	37174, 44642	14144
4	$[Ni(bz)_2(phen)Cl_2].H_2O$	32679, 40983	15037
5	$[Ni(bz)(bipy)Cl_2]$	37313, 44242	19157
6	$[Zn(bz)_2(en)(NO3)_2].6H_2O$	37031	LMCT

Table 5. The electronic solid reflectance spectral data of mixed ligand nickel(II), copper(II) and zinc(II)complexes of benzaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine

S/N	Compounds	π_3-π_4/charge transfer	d-d transition
1	$[Cu(bz)_2(bipy)(NO_3)_2]$	33783, 39525	13140
2	$[Cu(bz)_2(en)(NO_3)_2].3H_2O$	33783, 39370	18148
3	$[Cu(bz)_2(phen)(NO_3)_2].6H_2O$	33783, 39682	14925
4	$[Ni(bz)_2(phen)Cl_2].H_2O$	32081, 39682	14925
5	$[Ni(bz)(bipy)Cl_2]$	33783, 39682	18518
6	$[Zn(bz)_2(en)(NO_3)_2].6H_2O$	39525	LMCT

Antimicrobial activities

The results are given in table 6. The nickel (II), copper (II) and zinc (II) complexes showed exceptional inhibitory activity at varying levels of concentrations with the exception of $[Ni(bz)(Bipy)Cl_2]$ which did not inhibit *Bacillus subtillis* and $[Ni(bz)_2(phen)Cl_2].H_2O$ which did not inhibit any of the fungi organism. The copper complexes showed pronounced inhibitory activity against the fungi tested, with the exception of $[Cu(bz)_2(bipy)(NO_3)_2].3H_2O$ which was resistant. Generally, the Ni and Cu complexes could be described to have more antifungal activity than antibacterial activity. Gentamycin and tioconazole served as positive control against bacteria and fungi respectively.

Table 6: Antimicrobial activity of mixed ligand nickel(II) and copper(II) complexes of benzaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine

Compounds	*E. coli*	*S. aureus*	*P. aer*	*B. subtillis*	*C.albicans*	*A. niger*	*P. notatum*
$[Cu(bz)_2(bipy)(NO_3)_2]$	30	28	25	30	R	R	R
$[Cu(bz)_2(en)(NO_3)_2].3H_2O$	10	10	15	10	36	40	25
$[Cu(bz)_2(phen)(NO_3)_2].6H_2O$	30	30	25	30	50	46	50
$[Ni(bz)_2(phen)Cl_2].H_2O$	34	31	30	30	R	R	R
$[Ni(bz)_2(bipy)Cl_2]$	15	10	10	-	30	32	15
$[Zn(bz)_2(en)(NO_3)_2]$	13	20	10	8	22	27	13
Gentamycin/Tioconazole	20	20	20	20	30	30	40
Methanol	R	R	R	R	R	R	R

S. aureus = Staphylococcus aureus; E. coli = Escherichia coli; P. aer =Pseudomonas aeruginosa, C.albicans = Candida albicans; A. niger = Aspergillus niger; P. notatum = Penicillium notatum

Conclusion

Mixed-ligand complexes of nickel(II), copper(II) and zinc(II) of Benzaldehyde with 2,2′-bipyridine, ethylenediamine and 1,10-phenanthroline were found to be six-coordinate octahedral in geometry as corroborated by magnetic susceptibility measurements, infrared and electronic spectral data. The in vitro nickel(II), copper(II) and zinc(II) complexes showed broad spectrum of antimicrobial activity against the Gram-negative, Gram-positive and fungi tested with $[Cu(bz)_2(phen)(NO_3)_2].6H_2O$ having outstanding activity which showed that the complexes are potential broad spectrum antifungal and antibacterial agent

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