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SYNTHESIS AND CHARACTERISATION OF MIXED-LIGAND MANGANESE (II) AND COPPER (II) COMPLEXES OF BENZALDEHYDE WITH 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE AND ETHYLENEDIAMINE

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Abstract

Manganese (II) and copper (II) complexes of benzaldehyde and their 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and ethylenediamine (en) were synthesised and characterised by metal analysis, infrared spectroscopy, electronic spectral studies and magnetic susceptibility measurement. The results of the magnetic susceptibility measurement, and electronic spectra inferred that the Mn (II) and Cu (II) complexes assumed octahedral geometries. Manganese (II) and copper (II) complexes were screened for *in vitro* antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, *Candida albicans*, *Aspergillus niger*, *Penicillium notatum*. The Manganese complexes showed more antibacterial and antifungal activity than the copper complexes except $[Mn(bz)(bipy)(Cl_2)(H_2O)]$ and $[Mn(bz)(en)(Cl_2)(H_2O)]$ which were not active against fungi.

Keywords : Benzaldehyde, Mixed ligand complexes, Magnetochemistry, Spectral, Antimicrobial activity

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Introduction

The role of metal ion in biological processes cannot be over-emphasized. For instance manganese and copper ions are involved in many vital biological processes and are required for the survival of all living organisms. They are found in all organisms, nearly exclusively as constituents of proteins, including enzymes (Abu-elWafa

and Issa, 1989). These metals and some of their complexes have been found to exhibit antimicrobial activities.

Considerable studies have also been done on mixed-ligand metal (II) complexes containing nitrogen, oxygen and sulphur donor ligands due to their diverse biological activities, such as Antifungal and antibacterial activities. This informed our choice of benzaldehyde (Alan, 2006) and

N-donor bidentate ligand which are oxygen and nitrogen donor ligands, respectively.

Benzaldehyde (C_6H_5CHO) is an organic compound consisting of a benzene ring with an aldehyde substituent. It is the simplest aromatic aldehyde and one of the most industrially useful. Benzaldehyde's odour and taste are so unique and basic that it, in itself, forms an organoleptic class (Alka *et al.*, 2011). Benzaldehyde is commonly employed as confer almond flavor to foods and scented products and sometimes used in cosmetics products.

Although a good number of metal complexes containing benzaldehyde derivatives are reported in literature, to our knowledge there are no report of mixed ligand complexes containing only benzaldehyde with bidentate ligands such as 2,2'-bipyridine, 1,10-phenanthroline and ethylenediamine. Thus, the aim of this work is to synthesise, characterise and carryout the antibacterial properties of manganese (II) and copper (II) mixed ligand complexes of benzaldehyde with nitrogen containing ligands.

Materials and Methods

Reagents and solvents

Reagents used include manganese (II) chloride trihydrate and copper (II) trihydrate, 1,10-phenanthroline, and 2,2'-bipyridine. They are of analytical grade were utilized without further purification.

Preparation of $[Mn(Bz)(bipy)(Cl_2)]$

This was prepared by drop wise addition of manganese (II) chloride (0.5492g, 2.775mmol) dissolved in 4 mL of distilled water into a mixture of 2,2'-bipyridine

(0.4334g, 2.775mmol) dissolved in 4 mL of methanol and benzaldehyde (0.283mL, 2.775mmol), the mixture was stirred for 1 hour. The precipitate obtained was filtered, washed with methanol and dried in vacuo. All the other complexes were prepared using similar procedure.

Preparation of $[Cu(bz)_2(bipy)(Cl_2)]$

This was prepared by drop wise addition of copper(II) chloride (0.4688g, 2.775 mmol) dissolved in 4 mL of distilled water into a mixture of 2,2'-bipyridine (0.4334g, 2.775mmol) dissolved in 4 ml of methanol and benzaldehyde (0.283mL, 2.775mmol), the mixture was stirred for 1 hour. The precipitate obtained was filtered, washed with methanol and dried in vacuo (Amer *et al.*, 2017). All the other complexes were prepared using similar procedure.

Antimicrobial Susceptibility Testing

The antimicrobial activity of the synthesized compounds was determined by disc diffusion method. The compounds were weighed and dissolved in 2.5 mL of methanol making a concentration of 25 mg/mL, from which serial dilution of about four more concentrations was prepared. A mass of the culture medium (Nutrient agar and Sabouraud Dextrose agar) was weighed and dissolved in distilled water.

The mixing was heated to homogenise and sterilised in an autoclave for 60 minutes which was then poured into a Petri dish and left to solidify. A colony from a 24 hours fresh culture of the various organisms was dissolved in 5 mL of sterile distilled water, which was spread on the prepared culture agar. Sizeable hole was bore on the culture plate and the different concentration of the complex was added into each hole. The Petri dishes were then incubated for 24 h

for bacteria and 72 h for fungi before the inhibition zone diameters was measured.

Physical measurements

The percentage metal (manganese and copper) in the prepared complexes was determined by complexometric titration using EDTA solution (Table 1) while the electronic spectra of the synthesized complexes were determined in methanol, chloroform and in solid state using Perkin Elmer Lambda 950 UV/VIS spectrophotometer in 1cm glass cell.

The infrared spectra of the free ligands and complexes were determined in the region $4000\text{--}400\text{ cm}^{-1}$ on Perkin Elmer spectrum 11 FT IR spectrophotometer using nujol.

The magnetic susceptibilities of the compounds at room temperature were measured using Sherwood magnetic susceptibility balance.

Results and Discussion

Magnetic moments

The effective magnetic moment of Mn (II) complexes is expected to be close to the spin-only value of 5.90 B.M. The ground term is ${}^6A_{1g}$ and there is no orbital contribution (Cotton *et al.*, 1999). Consequently, the observed moment in the range 4.5–5.95 BM for the Manganese complexes indicates that it is high spin and complementary of octahedral geometry. A lower moment of 4.5 B.M. for $[\text{Mn}(\text{bz})_2(\text{en})(\text{Cl}_2)(\text{H}_2\text{O})]$ indicates dimerisation (George, 1995). A moment of 1.9–2.2 B.M. is usually observed for mononuclear copper (II) complexes, regardless of stereochemistry (Harbatsevich *et al.*, 2015). The magnetic moment of the copper (II) complexes fall between 2.17–2.30 B.M. expectedly higher than the spin only moment due to orbital contribution and spin-orbit coupling.

Table 1: Analytical and physical data of manganese (II) and copper (II) complexes of benzaldehyde

Compounds	Mol. wt. (g mol^{-1})	Colour	M.pt($^{\circ}\text{C}$)	% Metal Exp (Cal)	μ_{eff} (BM)
$[\text{Cu}(\text{bz})_2(\text{phen})(\text{Cl}_2)] \cdot 2\text{H}_2\text{O}$	526.86	Green	> 300	11.00 (11.28)	2.17
$[\text{Cu}(\text{bz})_2(\text{bipy})(\text{Cl}_2)] \cdot 3\text{H}_2\text{O}$	502.84	Green	> 300	11.19 (11.40)	2.16
$[\text{Cu}(\text{bz})_2(\text{en})(\text{Cl}_2)] \cdot \text{H}_2\text{O}$	406.75	Blue	260–262	14.92 (14.94)	2.30
$[\text{Mn}(\text{bz})(\text{phen})(\text{Cl}_2)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	412.18	Yellow	> 300	10.32 (10.93)	5.89
$[\text{Mn}(\text{bz})(\text{bipy})(\text{Cl}_2)(\text{H}_2\text{O})]$	388.15	Cream	> 300	13.87 (13.52)	5.95
$[\text{Mn}(\text{bz})_2(\text{en})(\text{Cl}_2)(\text{H}_2\text{O})]$	292.07	Brown	240–242	18.81 (19.13)	4.50

Infrared Spectra

The $\nu(\text{C}=\text{O})$ vibration in benzaldehyde was observed at 1704 cm^{-1} (Table 2). This band shifted to $1567\text{--}1689\text{ cm}^{-1}$ in the metal (II) complexes due to coordination

of the O donor atom of the aldehyde group (Hood and Skaar, 2012) and the two bands in the range of $2853 \div 2923\text{ cm}^{-1}$ are characteristic of the $(=\text{C}-\text{H})$ stretch of the aldehyde group (Omoriegie and Wood, 2011).

The bands in the range 3229-3326 cm^{-1} can be referred to as the N-H vibration of the ethylenediamine ligand (Osowole *et al.*, 2012). The spectra of 1,10-Phenanthroline and 2,2'-Bipyridine exhibit a strong band in the range of 1457-1589 cm^{-1} region due to the $\nu(\text{C}=\text{N})$ (Patel and

Woods, 1990). The bands appearing at 680-560 and 463-492 cm^{-1} for $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations in spectra of the Mn (II) and Cu(II) complexes indicated that the metal ions and organic ligands were coordinated (Roeges, 1998).

Table 2: Relevant Infrared bands (cm^{-1}) of manganese(II) and copper(II) complexes of benzaldehyde

Compound	$\nu(\text{C}=\text{O})_{\text{str}}$ (cm^{-1})	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{C}\pm\text{H})$ (cm^{-1})	$\nu(\text{M}\pm\text{O})$ (cm^{-1})	$\nu(\text{M}\pm\text{N})$ (cm^{-1})
bz	1704s	-		-	-
$[\text{Cu}(\text{bz})_2(\text{phen})(\text{Cl}_2)].2\text{H}_2\text{O}$	1625	1584	853vs, 720vs	644	464
$[\text{Cu}(\text{bz})_2(\text{bipy})(\text{Cl}_2)].\text{H}_2\text{O}$	1600	1566	776s	659	475
$[\text{Cu}(\text{bz})_2(\text{en})(\text{Cl}_2)].\text{H}_2\text{O}$	1567	1457		680	475
$[\text{Mn}(\text{bz})(\text{phen})(\text{Cl}_2)(\text{H}_2\text{O})].2\text{H}_2\text{O}$	1689	1589	852s, 729s	546	474
$[\text{Mn}(\text{Bz})(\text{bipy})(\text{Cl}_2)(\text{H}_2\text{O})]$	1603	1574	773vs	626	463
$[\text{Mn}(\text{Bz})(\text{en})(\text{Cl}_2)(\text{H}_2\text{O})]$	1622	1514		592	492

Electronic Spectra

The electronic spectra in methanol, chloroform and solid reflectance data of the complexes are presented in Table 3. The charge transfer and $\pi \rightarrow \pi^*$ transitions of the synthesised complexes were observed in the range of 38619-44643 and 33445 - 33898 cm^{-1} region respectively.

An octahedral Mn (II) complex is usually characterised by three weak absorption bands due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$, and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ transitions (Sharma *et al.*, 2012). The manganese complexes only showed one of these transitions at 14925 cm^{-1} for $[\text{Mn}(\text{Bz})(\text{bipy})(\text{Cl}_2)(\text{H}_2\text{O})]$ assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$, 24875 cm^{-1} for $[\text{Mn}(\text{Bz})(\text{phen})(\text{Cl}_2)(\text{H}_2\text{O})].2\text{H}_2\text{O}$ assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ and 11467 cm^{-1} for $[\text{Mn}(\text{Bz})(\text{en})(\text{Cl}_2)(\text{H}_2\text{O})]$ assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$.

It has been found from literature that coordinating solvent have an effect on

spectra of copper (II) complexes. When the band positions remain unchanged in coordinating and non-coordinating solvent it indicates an octahedral geometry (Veysel *et al.*, 2002).

The electronic spectra of the synthesised copper(II) complexes in chloroform exhibited one broad d-d transition at 14006, 13928 and 14925 cm^{-1} for $[\text{Cu}(\text{bz})_2(\text{bipy})(\text{Cl}_2)]$, $[\text{Cu}(\text{bz})_2(\text{phen})(\text{Cl}_2)]$ and $[\text{Cu}(\text{bz})_2(\text{en})(\text{Cl}_2)]$ respectively. These bands also appeared in methanol which is in conformity with octahedral configuration of copper. The proposed structures of the complexes are as presented (Figure 1).

Antimicrobial Activities

The antimicrobial activities of manganese and copper complexes were carried out on seven microorganisms, which include 4

Table 3: Relevant electronic solution and solid reflectance spectra of manganese (II) and copper (II) of benzaldehyde

Sample	CT (cm ⁻¹)			$\pi - \pi^*$ (cm ⁻¹)			d-d (cm ⁻¹)		
	CHCl ₃	MeOH	Solid	CHCl ₃	MeOH	Solid	CHCl ₃	MeOH	Solid
[Cu(bz)(bipy)(Cl ₂)].3H ₂ O	40984	42553	39683	33784	33445	33784	14006	13947	13514
[Cu(bz)(phen)(Cl ₂)].2H ₂ O	40984	44643	39683	33898	33838	33784	13928	13850	14044
[Cu(bz)(en)(Cl ₂)]H ₂ O	40984	42553	39683	37175		31949	14925	14948	14903
[Mn(bz)(bipy)(Cl ₂)(H ₂ O)]	-	42553	39683	-	35461	33784	-	18552	14925
[Mn(bz)(phen)(Cl ₂)(H ₂ O)].2(H ₂ O)	-	43860	39683	-	35211	33784	-	18552	24875
[Mn(bz)(en)(Cl ₂)(H ₂ O)]	-	38619	39370	-	37879	33784	-	18552	11467

bacteria (*Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*) and 3 fungi (*Candida albicans*, *Aspergillus niger* and *Penicillium notatum*) using agar diffusion methods.

Different concentrations of the complexes were prepared and used for the test and the zones of inhibition of the organisms. Methanol was used as the negative control while Gentamycin (for bacteria) and Tioconazole (for fungi) were used as the positive control. Copper complexes showed low zone of inhibition for bacteria but high zone of inhibition for fungi (Table 4). Copper complexes were more active than Tioconazole for *Candida albicans* and the Manganese complexes showed large zone of inhibition for bacteria, but only [Mn(Bz)(phen)(Cl₂)(H₂O)].2H₂O showed high zone of inhibition for fungi, while [Mn(Bz)(bipy)(Cl₂)(H₂O)] and [Mn(bz)(en)(Cl₂)(H₂O)] had no activity against fungi. The Manganese complexes were generally more active than gentamycin against the bacteria while

[Mn(Bz)(phen)(Cl₂)] was more active than Tioconazole against *Candida albicans* and *Penicillium notatum*.

Conclusion

The reaction of MnCl₂ and CuCl₂ with benzaldehyde and 1,10-Phenanthroline, 2,2'-Bipyridine and ethylenediamine yielded mixed ligand complexes. The complexes formed were characterised by metal analysis, IR, Magnetic susceptibility and UV-VIS spectroscopy and probable six coordinate octahedral geometry is suggested for all the compounds. Screening of the complexes for *in vitro* antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, *Candida albicans*, *Aspergillus niger*, *Penicillium notatum*, the Manganese complexes displayed promising antibacterial and antifungal properties except [Mn(bz)(bipy)(Cl₂)(H₂O)] and [Mn(bz)(en)(Cl₂)(H₂O)] which had no activity against fungi.

Figure 1: Proposed structure of complexes Synthesized

Table 4: Antimicrobial activities of manganese (II) and copper (II) complexes of benzaldehyde

Sample	Diameter of zones of inhibition (mm)						
	E.c	S.a	Ps.a	B.s	C.a	A.n	P.en
[Cu(bz)(bipy)(Cl ₂)].3H ₂ O	12	14	10	18	32	30	40
[Cu(bz)(phen)(Cl ₂)].2H ₂ O	14	10	22	34	42	14	30
[Cu(bz)(en)(Cl ₂)].H ₂ O	12	R	14	R	30	32	36
[Mn(bz)(bipy)(Cl ₂)(H ₂ O)]	30	36	22	30	R	R	R
[Mn(bz)(phen)(Cl ₂)(H ₂ O)].2(H ₂ O)	34	28	12	32	34	34	42
[Mn(bz)(en)(Cl ₂)(H ₂ O)]	14	10	10	12	R	R	R
Gentamycin/Tioconazole	18	18	16	20	14	40	20
Methanol	R	R	R	R	R	R	R

S.a = *Staphylococcus aureus*, E.c = *Escherichia coli*, B.s = *Bacillus subtilis*, C.a = *Candida albicans*, A.n = *Aspergillus niger*, Pen=*Pennicillin notatum*, R = Resistant *Pennicillin notatum*.

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