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PHYSICOCHEMICAL STUDIES OF MANGANESE (II) AND COPPER (II) COMPLEXES AND THEIR ADDUCT

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ABSTRACT

Bis(salicylaldehydato) manganese (II) and Bis(4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedionato) copper(II), their 2,2'-bipyridine, ethylenediamine, 1,10-phenanthroline and tetramethylethylenediamine adducts have been synthesized and characterized by metal analysis, FT-IR, UV–Visible, magnetic susceptibility and antimicrobial activity. The complexes and adducts were obtained as brown, yellow or light green colour. The metal analyses were in close agreement with the theoretical values expected. The infrared spectra of the manganese(II) complex revealed the coordination of salicylaldehyde through the carbonyl group and the hydroxyl group, while 2,2'-bipyridine, ethylenediamine, 1,10-phenanthroline and tetramethylethylenediamine coordinated to the metal through the nitrogen atoms. The magnetic moment data suggests low-spin octahedral geometry for $[Mn(sal)_2(H_2O)_2]$ (μ_{eff} = 2.14 B.M), high-spin octahedral geometries for $[Mn(sal)_2(en)].5H_2O$ (μ_{eff} = 5.50 B.M), $[Mn(sal)_2(phen)]$ (μ_{eff} = 6.2 B.M),$[Mn(sal)_2bipy]$(μ_{eff} =5.95 B.M) and $[Mn(sal)_2(tmen)]$(μ_{eff} =5.98 B.M.). The electronic measurements are indicative of a probable four-coordinate square planar geometry for $[Cu(tfnb)_2]$ while five-coordinate square pyramidal geometry are proposed for the copper(II) adducts. The complexes and adducts were screened against various bacteria and fungi. The copper complex and adducts were moderately active against fungal strain except $[Cu(tfnb)_2]$ and $[Cu(tfnb)_2en]$ in Aspergillus niger which showed pronounced activity and resistance respectively.

Keywords: *Salicylaldehyde, 4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedione, Magnetochemistry, antimicrobial activity*

INTRODUCTION

Mixed-ligand complexes of transition metals are involved in different biological processes; they have significant applications in analytical and other branches of Chemistry (Prasad *et al*., 2002; Mahdi *et al*., 2017). Literature has revealed that aldehydes can function as ligands in transition metal complexes and they are very important functional group in organic Chemistry(Huang and Gladysz, 1988).Salicyaldehyde and its derivatives are of great interest in coordination chemistry and have been studied extensively because of their strong coordinating ability and their complexes have found application in both pure and applied chemistry (Agrawal *et al*., 2012).The in vitro antibacterial studies of the ligands and the metal complexes have also been carried out and the complexes have been found to be more potent bactericides than the ligands(Agrawal *et al*., 2012).

Several applications of metal complexes have been reported(Butler *et al*., 2015; Lehner *et al*., 2014; Campelo *et al*., 2006).Copper complexes with 1,10-phenantroline and 2,2-bipyridine have been described to cleave DNA and inhibit tumoral cell growth.

In a study, the cytotoxicity activity of copper (II) complex of the type [Cu(O–O)(N–N)X], where O–O = 4,4,4-trifluoro-1-phenyl-1,3-butanedione, 1-(4-chlorophenyl)-4,4,4-trifluoro-1,3-butanedione or 2-thenoyltrifluoroacetone was shown to inhibit the growth of K562 cells with the 1,10-phenanthroline compounds exhibiting more ability to inhibit the growth of chronic myelogenous leukemia cell line (Almeida *et al*; 2015).In Vitro anticancer activity of five cationic platinum(II) complexes of general formula, [Pt(NH_3)$_2$-(β-diketonate)]X where X is a non-coordinating anion and β-diketonate = acetylacetonate, 1,1,1-trifluoroacetylacetonate, benzoylacetonate, 4,4,4-trifluorobenzoylacetonate was reported by Wilson and Lippard; 2012.

Literature have reported metal(II) complexes with salicylaldehyde/4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedione(Postmos*et al.,*1966; Farzin *et al*., 2008; Omoregie *et al*; 2016; Mahdi *et al.,* 2017; Hema *et al*; 2019) but there is dearth of information of manganese (II) complex of salicylaldehyde/copper(II) of 4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedione with nitrogen donors such as 2,2'-bipyridine, ethylenediamine, 1,10-phenanthroline and tetramethylethylenediamine. Hence, the need to synthesise and characterise these compounds and determine their biological properties.

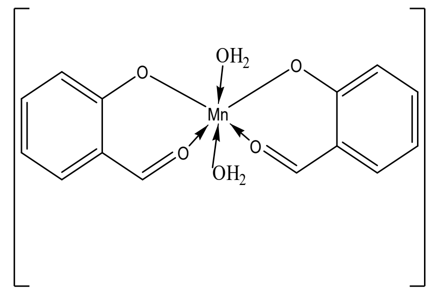
MATERIALS AND METHOD

Reagents and solvents

All the chemicals used were of reagent grade. The reagents used include; copper nitrate, 1,10-phenanthroline, 2,2'-bipyridine, ethylenediamine, salycylaldehyde, manganous acetate, $ZnSO_4.7H_20$, ammonia/ammonium chloride (NH_3/NH_4Cl), solochrome indicator, nitric/perchloric acid (1:1). Solvents used include methanol, acetone, distilled water, diethyl ether, chloroform, hexane, EDTA.

Preparation of [Mn(sal)$_2$(H_2O)$_2$] (1:2)

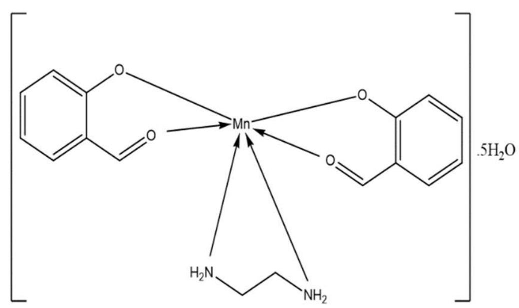
Manganous acetate (0.83 g, 0.003 mol) was weighed and dissolved in 4mL methanol and stirred for about 15 minutes. (1.16 mL, 0.006 mol) of salicylaldehyde was added and the mixture stirred for 1 hour, 15 minutes. The resulting light blue precipitate was filtered, washed with methanol and dried.



[Mn(sal)$_2$(H_2O)$_2$]

Preparation of [Mn(sal)$_2$(en)].5H_2O (1:2:1)

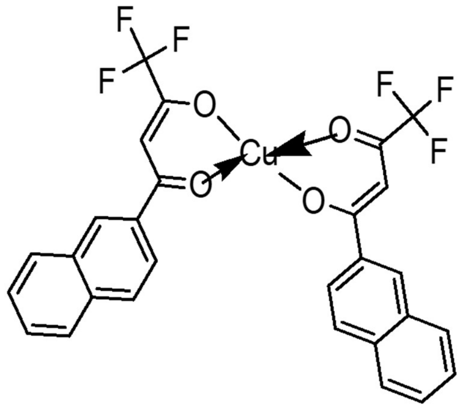
Manganous acetate (0.83 g, 0.003 mol) was weighed and dissolved in 4mL methanol and stirred for about 15 minutes. (1.16 mL, 0.006 mol) of salicylaldehyde was added and stirred for 30minutes. (0.227 mL, 0.003 mol) of ethylenediamine (en) was added and the mixture was stirred for 45 minutes. The resulting brown precipitate was filtered, washed with methanol and dried. Similar procedure was used for the preparation of the phenanthroline complexes.



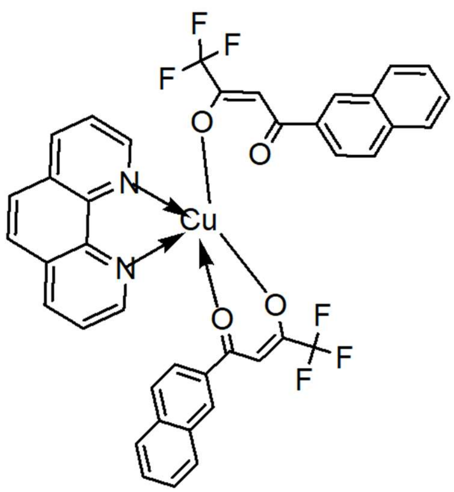
[Mn(sal)$_2$(en)].5H_2O

Preparation of [Cu(tfnb)$_2$] (1:2)

A solution of $CuCl_2{\cdot}6H_2O$ (0.228 g, 0.94 mmol) in water (1.2 mL) was added to4,4,4-trifluoro-1-(2-napthyl) 1,3-butanedione (0.50 g, 1.88mmol) in methanol (5 mL). The mixture was stirred for one hour and 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 2,2′-bipyridine and ethylenediamine adducts.



$Cu(tfnb)_2$



$Cu(tfnb)_2$phen

Physical measurement

The percentage metal was determined by titrimetric method using EDTA and solochrome indicator, while the IR Spectra were recorded in the range 4000-400cm^{-1} using KBr on Perkin Elmer II FT-IR Spectrometer. UV-Vis spectra of the samples were measured in the region 190-900cm^{-1} using a Perkin Elmer Lambda 950 UV-Vis spectrometer. Magnetic susceptibility of the samples was measured with a Sherwood Scientific magnetic susceptibility balance, MSB Mark 1. Melting points of the complexes were determined by Stuart melting point apparatus. All physical measurements were done in the Department of Chemistry, University of Ibadan, Nigeria.

RESULTS AND DISCUSSIONS

The colour, melting point and percentage yield are presented in Table 1. The melting point of the complexes melted within the range of 117-283^{o}C.All the complexes were soluble in methanol but insoluble in acetone.

Magnetic moments

The room temperature magnetic moments for the synthesized complexes range from 5.50-6.27 BM which is consistent with high spin octahedral stereochemistry except $[Mn(sal)_2(H_2O)_2]$ with magnetic moment of 2.14B.M, which is consistent with low spin octahedral geometry (Syiemlieh *et al*., 2018).A moment of 1.73-2.2 B.M. is usually observed for magnetically dilute copper(II) compounds (Patel and Woods., 1990). The copper(II) complex and adducts had moments in the range 1.71-2.00 B.M.

Infrared Spectra

The relevant infrared spectra data of the prepared Mn(II) and Cu(II) complexes prepared are presented in Table 2 and 3 respectively. In some of the complexes, O-H bands were observed in the range 3445-3399cm^{-1}, this indicates the presence of water molecules either as water of crystallization in the lattice structure. In the spectrum of salicylaldehyde, the observed band at 1666cm^{-1} is attributed to (C=O+C=C) stretching vibration. There was a lower frequency shift upon complexation (1666cm^{-1}→1639cm^{-1}), which indicates that salicylaldehyde coordinated through the carbonyl oxygen (Omoregie *et al*., 2016).

Table1: Analytical and physical data of manganese(II), copper(II) complexes and adducts.

Compounds	Mol. wt. (g mol^{-1})	Colour	M.pt (^{o}C)	%Metal Exp (Cal)	Yield %	μ_{eff} (BM)
[Mn(sal)$_2$(H$_2$O)$_2$]	333.17	Light green	117-119	17.3(16.5)	73.7	2.14
[Mn(sal)$_2$(phen)]	356.18	Yellow	154-156	10.99(11.5)	36.33	6.27
[Mn(sal)$_2$bipy]	453.06	Orange	164-166	12.25(12.12)	37.7	5.95
[Mn(sal)$_2$(en)].5H$_2$O	471.38	Brown	273-274	11.77(11.65)	46.3	5.50
[Mn(sal)$_2$(tmen)]	413.13	Dark green	220*	13.01(13.29)	94.6	5.98
[Cu(tfnb)$_2$]	593.99	Light green	280-283	8.98(9.05)	35.2	1.74
[Cu(tfnb)$_2$Phen]	792.21	Green	269-271	8.40(8.21)	27.8	1.75
[Cu(tfnb)$_2$Bipy]	750.18	Green	270-272	8.41(8.47)	26.3	2.00
[Cu(tfnb)$_2$en]	654.09	Light green		9.30(9.72)	37.2	1.71

Table 2: Selected IR Absorption bands(cm^{-1}) of manganese(II) complex of salicylaldehyde and adducts.

Complex	υ (O-H)	υ(C=O)+ υ(C=C)	□$_{s}$(C-H) phen/bipy
Sal		1666s, 1647w, 1621s, 1580vs	
[Mn(sal)$_2$(H$_2$O)$_2$]	3445s	1639s	
[Mn(sal)$_2$(phen)]	3267s	1650s, 1579m, 1527m	845vs, 730vs
[Mn(sal)$_2$(en)].5H$_2$O	3399s	1635s, 1598m	
[Mn(sal)$_2$(tmen)]	3360b	1649s,1570s	
[Mn(sal)$_2$(bipy)]	3390s	1671*,1640,1634*,1599vs,1574 vs, 1528vs, 1517*	773vs 756vs

S=strong, M=medium, W=weak, and Vs=very strong

Higher frequency shifts were observed on adduct formation except [Mn(sal)$_2$(en)].5H$_2$O which had lower frequency shift.C-H deformation bands δ(C-H) for the phenanthroline adduct was observed at around 849 cm^{-1} and 723cm^{-1} (Woods *et al*.,2009).

In the copper complexes, bands in the 1605-1509cm^{-1}was assigned as □$_{as}$(C=O)□□$_{as}$(C=C), while most of these bands are strong in [Cu(tfnb)$_2$] and they occurred as multiple bands. Upon adduct formation, hypsochromic shifts were observed in the □$_{as}$(C=O)□□$_{as}$(C=C) vibrations in all the adducts relative to the parent complex except [Cu(tfnb)$_2$Bipy].CH deformation bands of 2,2′-bipyridine were observed as strong bands in the

760-762cm^{-1} region while the phenanthroline adducts bands were observed around 721-726cm^{-1} and 850-866 cm^{-1} region. Coupled M-O and M-N stretching vibrational modes occurred in the range 420-696 cm^{-1} in the 2,2′-bipyridine and 1,10-phenanthroline adducts (Patel and Woods., 1990).

Electronic Spectra

The solid reflectance spectra of the Mn(II) complex and adducts are presented in Table 4.

Table 4: Relevant electronic solid reflectance spectra of Manganese(II) complex of salicylaldehyde and adducts.

Complexes	Absorption (c-m^{-1})	Transition
$[Mn(sal)_2(H_2O)_2]$	40,000	CT/ π- π
	32,258	π- π
	25,641	$^6A_{1g} \rightarrow {}^4E_{g,}$
	20,557	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	15,432	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
$[Mn(sal)_2(phen)]$	46,729	CT/ π- π
	31,847	π- π
	20,557	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	14,749	$^6A_2g \rightarrow {}^4T_{1g}(G)$
$[Mn(sal)_2(en)].3H_2O$	32,786	π- π
	25,510	$^6A_{1g} \rightarrow {}^4E_g$
	26,315	$^6A_{1g} \rightarrow {}^4E_g$
	15,432	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
$[Mn(sal)_2(tmen)]$	38,462	CT/ π- π
	31,646	π- π
	15,528	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	14,684	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
$[Mn(sal)_2(bipy)]$	38,462	CT/ π- π
	33,333	π- π
	20,000	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	15,385	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	14,706	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$

CT = Charge transfer.

The d-d transitions in the Mn(II) complexes are both spin as well as laporte forbidden (Syiemlieh *et al*.,2018), and hence, they have very weak intensity. In the spectra of the prepared Mn(II) compounds, the bands in the range 14,684-20,557 cm^{-1} have been assigned as $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ while the bands in the range 25,510-25,641 cm^{-1} have been assigned as $^6A_{1g} \rightarrow {}^4E_g$.

The electronic spectra of tfnb, the copper(II) complex and adducts in chloroform and methanol are presented in Table 5.

The ultraviolet spectra of the compounds are characterised by four peaks at 28,986-30,120, 33,223-34,364, 37,037-41,322 and 43,103-49,020 cm^{-1} assigned as n-□*/□-d, □$_3$-□$_4$*, Benzenoid band/σL-3dxy/□-□ (bipy.phen) and □$_3$-□$_5$*respectively.

Table 5: Relevant electronic solution spectra of copper(II) complex of 4,4,4-trifluoro-1-(2-napthyl)1,3-butanedione and their 2,2′-bipyridine, ethylenediamine and 1,10-phenanthroline

Tfnb	[Cu(tfnb)$_2$]	[Cu(tfnb)$_2$Phen]	[Cu(tfnb)$_2$Bipy]	[Cu(tfnb)$_2$en]	Tentative Assignment
Methanol 46,948	46,512	46,083 43,103		46,512	$\square_3$-$\square^*_5$
40,161	37,594	38,610		37,594	Benzenoid band/σ_L-3d_{xy}/□-□ (bipy.phen)
34,247	33,333	33,445	33,223	33,670	$\square_3$-$\square^*_4$
30,120	29,851	29,326	29,499	29,851	n-□*/□-d
	14,903	15,576	16,000	14,993	d-d
Chloroform 47,847			49,020		$\square_3$-$\square^*_5$
39,370 37,453	37,313	37,037	41,322	37,313	Benzenoid band/σ_L-3d_{xy}/□-□ (bipy.phen)
34,364	34,364	34,129	33,445	33,670	$\square_3$-$\square^*_4$
28,986	29,586	29,069	29,586	29,851	n-□*/□-d
	15,129	13,444	14,225	14,493	d-d

Literature has shown the different theoretical researches carried out on the ligand field spectra of copper(II) β-diketonates (Fackler and Cotton, 1963; Fackler *et al*; 1963a; Fackler *et al.,*1968; Johnson and Thornton, 1975) and it has been found that when there is lower frequency shift of d-d band on changing from a non-coordinating solvent (chloroform) to a coordinating solvent(methanol), it indicates a probable transformation from four-coordinate square planar copper(II) environment to five-coordinate environment (Woods *et al.* 2009; Omoregie *et al.,* 2014) and when a higher frequency is observed in coordinating solvent relative to non-coordinating solvent it indicates transformation from an original five-coordinate, square pyramidal geometry to a six-coordinate environment upon coordination of such solvent as methanol. Therefore, [Cu(tfnb)$_2$] is probably a square planar while the adducts are square pyramidal in geometry.

Antimicrobial Activity

The antimicrobial activities of manganese(II) and copper(II) complexes and adducts are presented in Tables 6 and 7 respectively.

Table 6: Antimicrobial Activities of Manganese(II) complex of salicylaldehyde and its Ethylenediamine, 1,10-Phenanthroline Adducts

Compounds	*P.aer*	*S.typhi*	*B.sub*	*S.aur*	*S.sp*	*E.coli*	*Ca*	*An*	*Rs*	*Pen*
[Mn(sal)$_2$(H$_2$O)$_2$]	-	-	-	-	-	22	-	-	-	20
[Mn(sal)$_2$(en)].5H$_2$O	-	-	-	-	-	-	20	40	-	20
[Mn(sal)$_2$(phen)]	30	18	24	36	32	30	26	22	14	18
Methanol	-	-	-	-	-	-	-	-		-
Gentamycin/ Ketoconazole	20	20	20	20	20	20	30	26	30	30

S.aur= Staphylococcus aureus, E.coli = Escherichia coli, B.sub= Bacillus substilis

P.aer= Pseudomonas aeruginosa, C.al= Candida albicans, A.nig= Aperginllus niger,

Pen= Pennicillin notatum. R.stol= Rhizopus notatum, S.sp =Streptococcus sp, S.typhi=Salmonellae typ

Table 7: Antimicrobial activity of the synthesized copper(II) compounds

Compounds	*S. aur*	*E. coli*	*B.sub*	*P. aer*	*S.typhi*	*K. pne*	*Ca*	*An*	*Pen*	*Rs*
Tfnb	26	24	20	26	24	22	20	18	14	16
[Cu(tfnb)$_2$]	24	24	24	24	20	18	18	16	18	16
[Cu(tfnb)$_2$Phen]	18	18	22	18	18	18	18	20	16	18
[Cu(tfnb)$_2$Bipy]	16	18	20	18	16	16	`16	14	14	16
[Cu(tfnb)$_2$en]	14	18	22	16	14	14	14	R	14	16
Gentamycin/ Ketoconazole	20	20	20	20	20	20	30	26	30	30
Methanol	No activities									

S. aur = Staphylococcus aureus ; B. sub = Bacillius subtilis; K. pne = Klebsiella pneumonia; E. coli = Escherichia coli; S.typi=Salmonella typhi; P. aer = Pseudomonas aeruginosa; Ca = Candida albicans; An =

Aspergillus niger ; Pen =Penicillium notatum Rs=Rhizopus stolonifer; *R= organism resistant to the extract; MS=organism moderately sensitive to extract; S=organism adequately sensitive to extract; ND=not done*

The antimicrobial activities of manganese (II) and copper(II) complexes and adducts were carried out and tested against ten microbial organisms using agar diffusion methods. Different concentrations of the compounds were used for the test and the zones of inhibition (mm) of the different organisms by the compounds were measured. Methanol was used as the negative control while Gentamicin and Ketoconazole were used as the positive control for the bacteria and fungi respectively. $[Mn(sal)_2(H_2O)_2]$ and $[Mn(sal)_2(en)].5H_2O$ showed resistance in all the bacteria except $[Mn(sal)_2(H_2O)_2]$ in *Escherichia coli* with pronounced activity while $[Mn(sal)_2(phen)]$ exhibited pronounced activity in all the tested bacteria except in *Salmonella typhi*. $[Mn(sal)_2(en)].5H_2O$ and $[Mn(sal)_2(phen)]$ showed pronounced activity on the tested fungi except $[Mn(sal)_2(phen)]$ in *Rhizopus stolonifer and Penicillium notatum* with moderate activity and $[Mn(sal)_2(en)].5H_2O$ in *Rhizopus stolonifer* which lacked antifungi activity. $[Mn(sal)_2(H_2O)_2]$ lacked antifungal activity in all the tested fungi except in *Penicillium notatum* with pronounced activity. The antibacterial and antifungal activity of $[Mn(sal)_2(phen)]$ compared favourably with Gentamycin/ ketoconazole used.

The tfnb and $[Cu(tfnb)_2]$ are active against all the bacteria tested but moderately active against the fungi except tfnb in *Candida albicans* with pronounced activity and $[Cu(tfnb)_2]$ in *Klebsiella pneumonia* with moderate activity. The copper adducts showed moderate activity in all the bacteria except in *Bacillius subtilis* in which they have pronounced activity. The copper adducts also showed moderately active on the fungi strains except $[Cu(tfnb)_2phen]$ and $[Cu(tfnb)_2en]$ in *Aspergillus niger* with pronounced activity and resistance respectively. The antibacterial activity of tfnb and $[Cu(tfnb)_2]$ compared favourably with Gentamycin used.

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