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SOLID STATE SYNTHESIS, CHARACTERIZATION AND ANTI-MICROBIAL STUDIES OF SOME TRANSITION METAL COMPLEXES OF A SCHIFF BASE LIGAND DERIVED FROM PARABENZOQUINONE AND GLYCINE

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ABSTRACT
Schiff base was synthesized by mixing parabenzoquinone and glycine mechanochemically. Its corresponding complexes ofCu, Co and Mn were synthesized by grinding metal (II) carbonates. The synthesized compound were characterized by elemental analysis, infrared spectroscopy, .melting/decomposition temperature determination and conductivity measurements .The infrared spectroscopic analysis of the ligand shows a peak at 1620cm^{-1} confirm the presence of azomethane while the shift to1602 cm^{-1},1623.15cm^{-1},1635.69cm^{-1} in Mn, Cu, Co complexes respectively confirmed bond formation from azo-group to metal. The melting point temperature of the ligand at 128.20^{0}C show that it is stable at low temperature while the decomposition temperature of Mn, Cu, Co complexes at 190^{0}C,188.4^{0}C,205^{0}C shows that they are stable .conductivity measurement shows that the complexes were found to be non-electrolytic as compared with the theoretical values.The ligand and its respective complexes showed antimicrobial activities against some bacteria and fungi at high concentrations (1000 µg/disc and 500 µg/disc) respectively while some showed no activity at all concentrations. However, Co complex shows significant activity against all the species at low concentration (250 µ/disc).
Key words: anti-microbial activity, parabenzoquinone, glycine, solid state synthesis.

INTRODUCTTION

Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient and economical technology (green chemistry), safety is largely increased, work up is considerably simplified, cost is reduced, increased amounts of reactants can be used in the same equipment, and the reactivities and sometime selectivities are enhance without dilution. Due to all these advantages there is an increasing interest in the use of environmentally benign reagents and procedures. The absence of solvents coupled with the high yields and short reaction time make the procedure of this work very attractive for the synthesis of coordination compounds (Kidwai, 2001). Mechanochemistry is a branch of chemistry which is concerned with chemical and physicochemical transformations of substances in all states of aggregation produced by the effect of mechanical energy (Kaupp, 2009).

Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes, because Schiff base complexes are potentially capable of forming stable complexes with metal ions, Many Schiff base complexes show excellent catalytic activity in various reaction at high temperature and in the presence of moisture. Over the past few years, there have been many report on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes. Metal complexes [Co(II), Cu(II) and Zn(II) ions] of Schiff base having played a central role in the development of co-ordination chemistry. Transition metal complexes have attracted curiosity due to DNA binding and cleavage properties under physiological conditions. Applications of metal complexes as chemical nucleases are the focus of current research. It has been demonstrated that in-organic complexes as chemical nucleases are the focus of current research. It has been demonstrated that inorganic complexes can be used in foot printing studies as sequence specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research(Xavier and Srividhya,2014).

Schiff base ligands are easily synthesized and form complexes with almost all metal ions. Over the past few years, there have been many reports on their applications in biology including antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial, antiviral activity and also as catalyst in several reactions such as polymerization reaction, reduction of thionyl chloride, oxidation of organic compounds, reduction reaction of ketones, aldol reaction, Henry reaction, epoxidation of alkenes, hydrosilylation of ketones, Diels–Alder reaction. The central metal ions in these complexes act as active sites for catalyzing chemical reactions such as oxidation of toluene. The controlled oxidation of toluene with H_2O_2 leads to a variety of products such as benzyl alcohol, benzaldehyde and benzoic acid which are industrially very important. $H_2O_2$is one of the most straightforward, clean, and versatile oxidants from both an environmental and economic perspective, because H_2O_2 has a high content of active oxygen and its byproduct is water (Menati *et al.,* 2016).

Recently, several groups used metal complexes as aprecursor for preparation of metal oxide nanoparticles by various methods. Considerable efforts have been dedicated to control the shape and size by different methods such as hydrothermal synthesis, microwave, chemical precipitation

and the solid-state thermal decomposition methods. Among various techniques for preparation of metal oxide nanoparticles, solid-state thermal decomposition of transition metal complexes is one of the best method, because it is inexpensive (economical) and does not use toxic solvent (pollution free and surfactant route and is much faster, whereas process conditions, particle size andpurity can be easily controlled (DehnoKhalaji, and Rahdari,2015).

Novel Schiff base of 4-aminoantipyrine with Biginelli adducts of salicylaldehyde has been designed and synthesized via Solid-state, metal complexes of this Schiff base with Ni(II),Zn(II),Cd(II) and Hg(II) metal ions were synthesised and characterised by elemental analysis, magnetic susceptibility, molar conductance, ESI mass, IR,NMR and UV-Vis spectral studies. The Ligand and its complexes have been screened for their in vitro antifungal and *in vivo* antibacterial activities against the fungi i.e., *Candida albicans, Aspergillus flavus, Pencillium spp., Aspergillus niger and Trichophyton* and the gram-negative bacteria *Escherichia coli, Vibrio spp., Pseudomonas aeroginosa, Vibrio parahaemolytics, Salmonella spp., Aeromonas spp., Klebsiella spp., Proteus spp.* and gram-positive bacteria *Bacillus spp* and *Staphylococcus aureus*. The in vitro antimicrobial activities of these metal complexes found to be stronger than the ligand (Rohini and Arul Antony 2016).

The synthesis of imidazole containing Schiff base ligands, the formation of their Ag(I) complexes and their activity against fungal pathogen, Candida albicans, is found to be problematic and the products are characterized by IR, NMR spectroscopic methods, micro-analysis, X-ray crystallography. Compared to the synthesis of the ligands the preparation of the Ag(I) complexes was simple and pure products were isolated in good yields. The Ag(I) complexes were also characterized using the same method as ligand. All of the Schiff base ligands and their corresponding Ag(I) complexes were tested for their anti-Candida activity(Theresa,2010).

The complexes of Copper(II), Nickel(II) and Cobalt(II) complexes two newly synthesized by grinding with the Schiff base, The Schiff bases ligands were synthesized by the condensation of 4,6-diacetyl resorcinol with 4-bromo aniline and 4-methoxy aniline. The ligands and their metal complexes are characterized by FTIR, Mass,^{1}H NMR, UV–Vis., elemental analysis, ESR and Thermal gravimetric analysis. Both The Schiff base and their metal complexes were tested for antimicrobial activity against gram positive bacteria *Staphylococcus aureus, Streptococcus pyogenes* and gram negative bacteria *E.scherichia coli, Pseudomonas aeruginosa* and fungus *Candida albicans, Aspergillus niger and Aspergillus clavatus* using Broth Dilution Method (Jignesh *et al.*,2014).

Coordination compounds of Cr(III), Ru(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions were synthesized from thefuran ligand [5-hydroxymethylfuran-2-yl-methyleneaminoquinolin-2-one] (H-MFMAQ) derived from the condensation of 5-hydroxymethylfuran-2-carbaldehyde and 1-aminoquinolin-2(1H)-one. Elemental analytical data, IR, NMR (1H, ^{13}C, and ^{15}N), EPR, XRD, SEM, TEM, EDX, TGA, mass, molar conductance, magnetic moment, and UV-Visible spectra techniques were used to confirm the structure of the synthesized chelates. According to the data obtained, the composition of the 1: 1 metal ions: furan Schiff base ligand was found to be $[M(MFMAQ)C_{l2}]$ (M = Cr(III) and Ru(III)) and $[M(MFMAQ)Cl(H_2O)]\cdot nH_2O$ in which (M =Mn(II); n = 1, Co(II); n = 0, Ni(II); n = 2, Cu(II); n = 0 and Zn(II); n = 2.5). The measurements of magnetic susceptibility, ligand field parameter, and reflectance spectra suggested an octahedral geometry for the complexes. Central metals ions and furan Schiff base coordinated viaO_3 andN donor sites which was observed from IR spectra. The cytotoxic activities of all inspected compounds were evaluated towards human breast *and lung cancer* cell *lines* (Amani *et al.*, 2018).

The synthesis of Co(II) and Cr(III) Schiff base complexes obtained from thiourea. The complexes were synthesized by template method and characterized by elemental analysis (CHNS), FT-IR, UV– vis spectroscopy, conductivity measurement and magnetic moment. The spectroscopic studies suggested the octahedral and square-pyramidal structures for Co(II) and Cr(III) complexes, respectively. Then the complexes were used as precursors for preparation of Co_3O_4 and Cr_2O_3nanoparticles via solid-state thermal decomposition without using a catalyst, toxic solvent, template or surfactant and complicated equipment, which makes it efficient, one-step, simple and environment-friendly. The chemical structure of the metal oxides is studied by FT-IR, XRD and SEM. To investigate the applications of the synthesized complexes, in the next step, the complexes were screened for antibacterial activity against clinically important bacteria such as Escherichia coli, Staphylococcus aureus, and Bacillus subtilis. The Cr(III) and Co(II) complexes showed good biological activity against all the tested bacteria. Also, the catalytic activities of the complexes were studied in toluene using non-toxic hydrogen peroxide as the oxidant. The results showed that Co(II) complex has catalytic activity for oxidation of toluene, but Cr(III) complex did not show any catalytic activity (Leila Kafiand, Leila Shirmohammadzadeh,2017).

The synthesis of selected cosmetic oligopeptides was performed manually, on the solid medium, using procedure of SPPS (solid phase peptide synthesis). The number of components and the composition of hydrogels have been developed individually, domestic pig skin was used. The degree of the skin hydration was measured with the SKINTEST plus camera, which uses the latest semiconductor technology (Beata *et al.,*2013).

This study was aimed at synthesizing Schiff base derived from benzophenone and glycine and their corresponding first row transition metal complexes Co (II), Mn(II) and Cu(II).

MATERIALSAND METHODS

Materials

The materials used were pestle and motor, Fourier Transform Infrared Spectrophotometer (FTIR-8400S), elemental analyser(Flash 2000 organic, University of Leeds), Jenway conductivity meter (model 4000), decomposition temperature (WRS-IB microprocessor melting apparatus),UV-visible (Jenway 6305 spectrophotometer)and all the chemical used are of analytical grade, the metals are obtained from their corresponding carbonate.

Method

Synthesis of ligand

para-benzoquinone (0.02mol) and glycine (0.02mol) were grinded in agate mortar for 5minutes and which resulted in the formation of p-benzoquinone-glycine ligand as a black colour which was dried in *vacuo* (Kidwai, 2001).

$$C_6H_4O_2 + NH_2CH_2COOH \longrightarrow C_8H_7O_3N + H_2O$$

Scheme 1: Synthesis of parabenzoquinone-glycine oxime ligand

$$C_8H_7O_3N + MCO_3 \longrightarrow [(C_8H_7O_3N)_2M] + CO_2$$

Synthesis of complexes

Metal carbonates (Mn, Co and Cu)(0.01mol) were grinded with the ligand (0.02mol) which resulted in the formation of a dark ash coloured complex of bis[p-benzoquinone -glycineoxime] Copper(II)**,**a dark purple coloured complex of bis[p-benzoquinone-glycineoxime]Cobalt(II)**,**dark brown or coffee coloured complex of bis[p-benzoquinone -glycineoxime] manganese(II).The complexes obtained were purified by recrystallization in ethanol and then dried in *vacuo* (Kidwai, 2001).

Scheme 2:General reaction for the synthesis of the complexes

Antimicrobial Activities

The bacterial strains used were *Escherichia Coli and Staphylococcus aureus,* prepared based on reported protocol.The complexes were dissolved separatel y in DMSO to have three different concentration s (50µg, 500µg and 1000µg) per disc. They were placed on the surface of the culture and incubated at 37°C for 24hours. Then, *in vitro* antibacterial activity of these complexes was carried out by paper disc diffusion method. The diameter of zone of inhibition produced by the complexes was compared with the standard (Cheesbrough, 2000 and Mukhtar., 2009).

RESULTS AND DISCUSSION

The interaction of glycine with parabenzoquinone formed Schiff base. The complexes were found to be coloured due to charge transfer

Table 1: IR Spectral DATA of the Metal (II) Complexes

FITR Value/ Samples	ν(M-N) cm^{-1}	ν(M-O) cm^{-1}	ν(C=N) cm^{-1}
$[(C_8H_6O_3N)_2Mn]$	512.12	415.31	1602
$[(C_8H_6O_3N)_2Cu]$	521.76	435.93	1623.15
$[(C_8H_6O_3N)_2Co]$	525.42	486.08	1635.69
Ligand			1620

Keys: M **=** Metal, ν **=** Wave number

The infra-red spectral result of the ligand para-benzoquinone-glycine-oxime shows a band at $1620cm^{-1}$ which is associated to v (C=N) stretching, while The complexes of para-benzoquinone-glycine-oxime with Manganese, Cobalt and Copper shows a band at $1602cm^{-1}$, $1635.69cm^{-1}$ and $1623cm^{-1}$ which are associated with their respective coordination with v(C=N) respectively, The absorption bands at $415.31cm^{-1}$, $486.08cm^{-1}$ and $435.93cm^{-1}$ which associated with v(M-O) respectively, $512.12cm^{-1}$, $525.42cm^{-1}$ and $521.76cm^{-1}$ which associated with v(M-N) respectively.
Comparing the bands in the ligand to that of the metal complexes shows that there is a shift in complexes to lower or higher frequencies which is an indication of complexation between the ligand and the metal ions, also in complexes new band appear due to v (M-O) and v(M-N) Which confirm complexation which are absent in ligand. The bands are compared with reported values by Reusch (1999).

Table 2: Decomposition temperature/melting point temperature and molarconductivity

Complexes	Decomposition/ Melting point Temp. (^oC)	Molar Conductivity ($\Omega^{-1}cm^2 mol^{-1}$)
$[(C_8H_6O_3N)_2Mn]$	190	35.2 0
$[(C_8H_6O_3N)_2Cu]$	188.4	40.80
$[(C_8H_6O_3N)_2Co]$	205	56.00
Ligand	128.2	

The interaction of glycine with para-benzoquinone resulted in the formation of para-benzoquinone-glycine oximeligands which is black in colour. The ligandpara-benzoquinone-glycine oxime melted with a melting point temperature of 128.2^oC.
The interaction of para-benzoquinone-glycine-oxime with respective divalent metal salts yield coloured complexes, the colour of the complexes is due to electronic transition from lower to higher energy level. Manganese, cobalt and copper complexes are dark brown (coffee), dark purple and greyish colour with decomposition temperature of 190^oC, 205^oC and $188.^oC$ respectively, the high decomposition temperatures of the complexes as compared to the ligand may be due the coordination between the central metal ion and the ligand.
Molar conductance measurement of the complexes (10^{-1}m) in DMSO solution were also determined which lies in the range of 29.0-60.6 $\Omega^{-1}cm^2 mol^{-1}$, the lower value indicate that they are non-electrolyte according to Sekhon *et al* (2010). The results are shown in table 2.
The elemental analysis result revealed that the percentage of nitrogen, carbon and hydrogen in thepara-benzoquinone-glycine-oxime are found to be N= 9.00%, C= 59.12%, H=5.00% respectively while the calculated percentage was found to be N= 8.48%, C= 58.18%,H= 4.27% respectively.
The elemental analysis result revealed that the percentage of nitrogen, carbon and hydrogen in para-benzoquinone-glycine-oxime complex of manganese are found to be 7.00%, 44.43% and 3.21% respectively, while the calculated are found to be 6.39%, 43.86% and 2.76% in respect of nitrogen, carbon and hydrogen, Cobalt complex be 5.98%, 42.90% and 3.03% respectively, while the calculated are found to

be 6.28%, 43.08% and 2.71% in respect of nitrogen, carbon and hydrogen, Copper complex 6.92%, 41.97% and 3.00% respectively, while the calculated percentage are found to be 6.15%, 42.20% and 2.66% in respect of nitrogen, carbon and hydrogen.elemental analysis conducted on both the ligand and its complexes confirmed the metal to ligand ratio in the complexes to be 1:2.

The solubility of Para-benzoquinone-glycine-oxime (ligand) and its corresponding metal complexes was also determined in different solvents, the ligand is soluble in acetone, ethanol and DMSO, but slightly soluble in methanol, water, diethyl ether, chloroform, but insoluble in n-hexane. The complexes are slightly soluble in ethanol, methanol, acetone, diethyl ether, chloroform, DMSO and water with the exception of Manganese complex which is soluble in ethanol, DMSO, and Copper complex is soluble in DMSO but insoluble in diethyl ether, Cobalt complex is also insoluble in diethyl ether, all the complexes are insoluble in n-hexane. Solubility depends on temperature, solvent i.e. those with similar polarity dissolve and also the type of solute. The relevance of solubility is to determine the suitable solvent that would be used to carry out other analysis such anti-microbial, conductivity measurement, UV-visible.

Table 3: Anti-Bacterial Activity, Anti-fungal Inhibition Zones

Complexes	Concentrations (µg/disk)	*E. coli*(mm)	*S. aureus*. (mm)	*C.*albicans (mm)	*A. flavus*(mm)
	250	15	19	10	0
	500	16	19	11	0
$[(C_8H_6O_3N)_2Mn]$	1000	18	20	15	0
	250	18	16	7	0
	500	18	17	10	0
$[(C_8H_6O_3N)_2Cu]$	1000	15	20	12	0
	250	12	12	10	0
	500	14	14	10	0
$[(C_8H_6O_3N)_2Co]$	1000	20	18	11	0
	250	0	0	11	8
	500	0	0	12	8
$[(C_{15}H_{12}O_2N)_2Co]$	1000	0	0	12	10
Ligand	250	16	10	0	0
	500	18	15	0	0
	1000	22	16	7	0
CONTROL (Genteamiecyin18µg/disk)		40	35		
CONTROL (Apron plus 10µg/disk)				38	20

Key:
E. coli = Escherichia Coli
S.aureus = Staphylococcus aureus
A .flavus= Aspergillus flavus
C. albicans= Candida Albicans

The antibacterial and antifungal screening test for the ligands and their metal (II) complexes were also determined. The inhibition zone (mm) was measured for all sample treated, some shows little or no activity as compare with Zahid*et al.,* 2000. Results are shown in table 3 above.

CONCLUSION

A new alternative method for synthesis of some Schiff base from para-benzoquinone with some amino acids is given, from available literature most of the Schiffbases and their complexes were synthesized via solution method Zahid *et al* (*2000*) But this research work is purely Mechanochemicalsynthetic method which was successful.

Schiff base was successfully synthesized via mechanochemical process using parabenzoquinone and glycine and their respective complexes were also synthesized.

The Schiff base was found to co-ordinate to the central metal atom through the nitrogen of the azomethane and the deprotonated oxygen of the amino acid. The elemental analysis result suggests the metal to ligand ratio to be (M: L) 1:2.

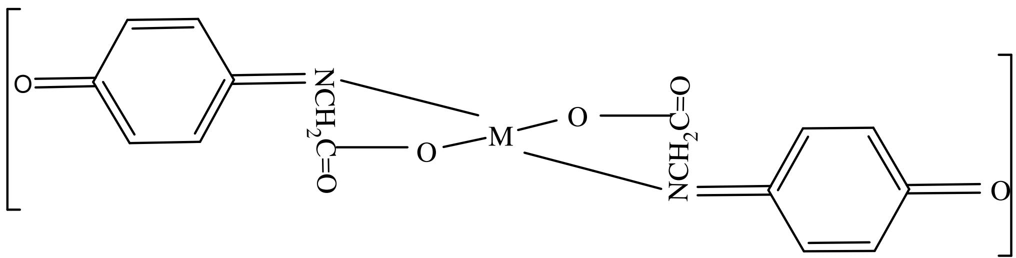

Figure 1: Propose structure of parabenzoquinone complexes

The antimicrobial result showed that all the complexes are active against C*. albicans*, E.*coli*,S. *Aureu*s but showed no activity against A.*flavus.*

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